PRINCIPLES OF
INORGANIC CHEMISTRY

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THIRD EDITION

New York
THE MACMILLAN COMPANY
LONDON: MACMILLAN & CO., LTD.
1906

Set up, electrotyped, and published January, 1903. Reprinted May, 1904; October, 1906.

Norwood Press
J. S. Cushing & Co. — Berwick & Smith Co.
Norwood, Mass., U.S.A.

PREFACE

INORGANIC CHEMISTRY within the last few years has undergone remarkable developments. This is due chiefly to generalizations which have been reached through physical chemistry. We can see most clearly what these developments are by comparing the inorganic chemistry of twenty years ago with that of to-day. Until recently the more important generalizations upon which the science of inorganic chemistry rested were: The conservation of mass and energy; the laws of definite and multiple proportions and combining weights; the law of Avogadro, and the periodic system. Inorganic chemistry was built upon these generalizations, and consisted largely in a description of the compounds formed as the result of the interaction of matter in terms of these laws. Relations between the composition and properties of compounds of different elements were pointed out, which were more or less deep-seated and far-reaching.

Within the last fifteen years several newly discovered generalizations have been added to those longer known, and some of these have been shown to be fundamental to the whole science of chemistry. The more important of these generalizations are: The theory of electrolytic dissociation; the law of mass action; the phase rule, and Faraday's law as the basis of chemical valence.

That these generalizations are of the very greatest importance for inorganic chemistry is obvious to any one who is familiar with the facts of physical chemistry and of inorganic chemistry. Take the theory of electrolytic dissociation, put forward by Van't Hoff and Arrhenius. We know to-day that nearly all inorganic reactions are reactions between ions; molecules and atoms as such having nothing to do with the reactions. They simply serve to furnish the ions, which are chemically the active agents. This obviously necessitates a fundamental change in our conceptions of chemical phenomena. It is not the uncharged atoms which react chemically, but these become chemically active only when they carry an electrical charge. The chemistry of atoms and molecules is thus largely replaced by the chemistry of ions.

Similarly, the law of mass action of Guldberg and Waage has produced a fundamental change in our method of regarding chemi-

cal reactions. It has not only shown that mass is an important factor in determining the magnitude of any given reaction, but in many cases can actually determine the direction of the reaction. In this law we have not simply a qualitative statement of the effect of mass, but a quantitative relation mathematically formulated.

The phase rule of Willard Gibbs has also played its part in the recent developments in inorganic chemistry. It has laid special stress upon the conditions of equilibrium between the different phases of the same and different substances, and has predicted the existence of unknown substances, many of which have recently been found. The phase rule is a beautiful, short-hand expression of great masses of facts, and it gives us a comprehensive grasp of these facts which without it would be impossible.

The application of Faraday's law as the basis of chemical valence is not a new conception, but the importance of this application has only recently become apparent. The importance of ions, which are charged atoms or groups of atoms, and the study of electrochemical phenomena in general have made prominent the fact that the law of Faraday is a fundamental law of chemistry as well as of physical chemistry. If we do not recognize this relation, the term "chemical valence" is without exact significance and meaning; when based upon the law of Faraday — a law to which thus far no exception is known — valence has an exact physical basis, and this is an important step for the development of chemistry.

The object of the present work is not to abandon the older generalizations, nor even the older methods of treating chemical phenomena in so far as they cannot be improved. On the contrary, the attempt has been made to retain those generalizations at their full value, and special stress is laid upon the periodic system, which has apparently fallen in certain directions somewhat into disrepute. This generalization reached by Lothar Meyer and Mendeléeff, which has been the philosophy of inorganic chemistry for so many years, and in terms of which so much has been discovered, is still of very great value. That it has serious defects no one can doubt; that these are far exceeded by its merits is strongly impressed upon the writer.

The aim of this book is to add to the older generalizations those recently discovered, and to apply them to the phenomena of inorganic chemistry in such a way that they may form an integral part of the subject, and, at the same time, be intelligible to the student. Why should we continue to teach the chemistry of atoms to students on the ground of its being a little simpler, perhaps, than the chem-

istry of ions, or on any other ground, if we know that it is not in accordance with the recently discovered facts? Or why should we continue to teach purely descriptive chemistry when the science of chemistry has outgrown this stage, and many of the most important relations have been accurately formulated in terms of the simpler mathematics?

These are questions which need only to be asked in order that their answer may be made apparent. If a student can grasp the conception of an atom and cannot add to this the idea of the atom carrying an electrical charge, his hope of ever learning anything of chemical phenomena in general is not bright.

The second point, the introduction of elementary mathematics into chemistry, may seem to be more serious. The earlier text-books on inorganic chemistry have been characterized by the absence of anything resembling a mathematical symbol, and chemistry has come to be known as a non-mathematical science. It is, however, obvious to any one who has traced the development of science that this condition of things cannot last. Physics has passed through the stages through which chemistry is now passing Faraday, the leading physicist of his day, was not a mathematician, but how different at present, when to be a physicist one must first be a fairly good mathematician. Indeed, it has been well said, that the state of development of any branch of natural science can be measured by the extent to which mathematical methods have been applied to it. That chemistry will become more and more mathematical is just as certain as that it will develop.

There seems to be no good reason why we should refrain for a moment from introducing simple, algebraic symbols into a comparatively elementary text-book in inorganic chemistry, where these best serve to bring out the relations between phenomena. They are introduced without question on almost every page of elementary works on physics, and have come to be taken as a matter of course. The same class of students, and frequently the same students, use these works and corresponding texts on chemistry. Why should chemists be hampered by being compelled to describe phenomena at length when these could be formulated in a single line? The time has come when they need not be, and the earlier elementary mathematics is introduced into text-books on chemistry, the better for chemistry and for the chemist.

The writer has refrained from introducing unproved theories and disputed questions as far as possible, since the student for whom this work is meant is scarcely at a stage to properly appreciate and

evaluate scientific discussion. The attempt has, however, been made to avoid dogmatism, since this is harmful even in an elementary work.

The physical properties of substances are described at much greater length than in the older works on inorganic chemistry. These usually follow the description of the chemical properties of the substance, and can, at the discretion of the teacher, be omitted in part or wholly if the student is not sufficiently advanced to properly appreciate their significance.

The methods of determining the molecular weights of dissolved substances are described briefly, since these problems, especially as connected with non-aqueous solvents, have become of fundamental importance in inorganic chemistry. The methods of measuring electrolytic dissociation are also discussed, and the conductivities and dissociation of a few of the best known acids and bases are given, since these furnish us with the best means of determining the relative strengths of these substances.

All experiments have been omitted from this work except in so far as they demonstrate important principles. This has been done to avoid breaking the continuity of the text; and since this work is meant primarily for students who are engaged in qualitative and quantitative analysis, it seems far better to leave instruction in the laboratory to works devoted especially to that purpose and to the teacher.

Should the present work contribute even a little towards the introduction of physical and physical chemical conceptions into chemistry, the writer will feel amply repaid for all his labor, since it is through these conceptions and apparently through these alone that we can hope to place chemistry among the exact sciences.

HARRY C. JONES.

PREFACE TO THE SECOND EDITION

THE short time that has elapsed since the appearance of the first edition of this work but serves to show how great a demand exists on the part of teachers and students of chemistry for the introduction of the recently discovered generalizations of physical chemistry into their science. We can now add to the description of reactions and substances formed as the final results of such reactions, certain of the laws which condition them and to which they in general conform. The final result will be a science of chemistry, not as exact, perhaps, as physics, but sufficiently exact to enable us to deal with many phenomena in terms of the simpler mathematics. This is the direction in which all branches of natural science are tending, and by which their state of development may be fairly gauged.

A large number of minor corrections and changes have been introduced into the second edition of this work. To most of these my attention has been called by a large number of friends, to whom I wish to take this opportunity to extend my hearty thanks.

It is to be hoped that any one who may discover an error in this edition will kindly communicate the fact to the author.

HARRY C. JONES.

PREFACE TO THE THIRD EDITION

The importance of physical-chemical generalizations for the teaching of general chemistry is now generally recognized. This is shown by the large demand for text-books of which these generalizations are made the basis, and by the increasing number of such works that are being produced.

The teaching of even elementary chemistry has been fundamentally modified in the light of these recently discovered relations, and teachers who desire to keep abreast with progress and to give their students the results of the latest and most fruitful developments, are becoming familiar with these relations and using them in the classroom. This applies to the colleges fully as much as to the universities.

The progress in this direction that has been made in the last ten years will probably be greatly outstripped during the next decade.

In this edition the atomic weights recommended by the International Committee for 1906 are used.

H. C. J.

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CHAPTER I

INTRODUCTION

The Study of Nature. — The study of nature is not limited to the world in which we live, but to the universe of which our world forms only a very small part. The study of the various aspects of nature, or natural science, forms the greatest and most comprehensive chapter of human knowledge. Indeed, so great is the field of natural science and so different the methods which are employed in studying nature, that no one mind can comprehend more than a small part of what has already been learned.

Natural science can, however, be subdivided into a number of branches, which are all related, but which possess inherent differences sufficient to distinguish the one from the other, and in some cases these differences are quite marked.

Astronomy has to do chiefly with the study of the motions and relations of bodies as a whole in the universe, while physics, chemistry, geology, and biology are concerned primarily with phenomena which manifest themselves on the earth. Of these, physics and chemistry are far more closely allied than they are to geology — the science of the formation of the surface of the earth, or to biology — the science of living matter.

Relations between Chemistry and Physics. — While it is impossible at this stage to give a comprehensive conception of the relations and differences between chemistry and physics, certain fundamental distinctions can be pointed out.

Connect a piece of copper with an electric battery, and an electric current will flow through it. The copper while carrying the current has properties which are different from copper through which no electricity is passing. Disconnect the copper from the electric battery, and it possesses its original properties.

Heat a piece of copper gently, and some of its properties are changed. It will give out heat to surrounding objects; it will

occupy a larger volume when hot than at ordinary temperatures. Allow the copper which has been warmed to cool, and it will possess again its original properties. Hammer the copper or bend it, and it will remain copper. Changes of this kind are known as physical.

If, on the other hand, we heat a piece of copper to redness in the presence of the air, a far more fundamental change takes place. The copper disappears and a black substance is formed which has properties quite different from the original copper. The black substance does not look like a metal. It cannot be drawn out into wire. It weighs considerably more than the original copper, and in general has properties sufficiently different from the original copper to show that we are dealing with an entirely different substance. If the black powder is now cooled to the original temperature of the copper, it retains its own characteristic properties.

It is obvious, therefore, that by heating to a sufficiently high temperature in the presence of the air, the copper has been transformed into something else, and that the new substance is not retransformed into copper when the original temperature is again restored.

The change effected in the latter case is, then, far more fundamental than in the former. While certain properties of the copper were changed by passing an electric current through it, or by gently warming it, these properties were restored again when the current was interrupted, or when the temperature was allowed to fall. The original copper remained copper. In the latter case, however, the *composition of the substance was changed*, and this is characteristic of chemical activity. The substances which react chemically lose many of their characteristic properties, and give rise to new substances with very different properties.

The distinction between physical and chemical change is not always as sharp as in the example given above. Certain phenomena manifest themselves which belong, strictly speaking, neither to chemistry nor to physics, but occupy a position midway between the two. A comparatively new branch of science which deals with these phenomena has come into prominence in the last fifteen years. This is known as physical chemistry.

Although the distinction between physical and chemical changes is not always a sharp one, yet, in most cases, there is no serious difficulty in deciding to which class a given set of phenomena belongs. In general, any change which does not affect the composition of substances is physical, while change in composition is characteristic of chemical transformations.

Elements and Compounds. — If we look about us, we recognize that nature is made up apparently of a great many substances. The soil and the rocks differ greatly in composition in different localities, and are always more or less complex. Water exists everywhere, and the air is a mixture of many substances. When we turn to living matter we find the complexity greatly increased. The simplest living being is composed of very complex substances, and the more highly developed organisms contain a countless number of substances.

This is the way the problem of the composition of the external world, as recognized by our senses, presents itself at first. It, however, becomes greatly simplified when we study the composition of things in a systematic and comprehensive manner. All known substances fall into two great classes, — those that cannot be decomposed into simpler substances and those that can. Take the piece of copper already referred to. By no process known to man can it be decomposed into anything simpler than copper. It can be caused to unite with other things and form substances more complex than copper, but deal with it as you will, and it cannot be decomposed into anything else. On the other hand, take the well-known substance water, add a little acid to it to make it conduct, and pass an electric current through it. The water will be decomposed into two simpler substances, both of them gases, and they will be set free the one at the one pole, the other at the other.

There is, therefore, a fundamental difference between copper and water — the one cannot be decomposed into simpler substances, the other can be decomposed into two substances, both of which differ fundamentally in their properties from the substance water.

Substances like copper which cannot be decomposed into anything simpler are known as *elements*, while those substances which can be decomposed into simpler things are known as *compounds*.

The Number of Elements and Compounds. — While the chemical compounds already known number more than a hundred thousand, the number of chemical elements which have thus far been discovered is only about seventy-five. When we consider that a compound is made up of two or more of these elementary substances, the whole problem of the composition of substances is vastly simplified. We can, then, refer every compound known, both in inanimate nature and in the realm of living matter, to a comparatively few elementary substances.

Take the rocks which are most familiar on the surface of the earth; they are made up chiefly of not more than a dozen elementary substances. In addition to this dozen elements they may contain a

number of other elementary substances, but these are present in relatively small quantities.

Water, which covers such a large portion of the surface of the earth, is, as we have seen, made up of two elements.

The atmosphere which is so essential to life is made up chiefly of two elements, containing, however, a number of other elements and compounds in relatively small quantities.

If we turn to living matter, we find a very large number of chemical compounds, and the greatest complexity represented. Cellulose, starch, albumen, are among the most complex substances known to the chemist, yet an analysis of these substances brings out the surprising fact that they contain scarcely more than a half-dozen elements.

The number of chemical elements known to us at present is, as already stated, about seventy-five. This number has been largely increased during the last few years, and there are good scientific reasons, as we shall learn, for believing that elements exist which have not yet been discovered. It should, however, be stated that if such elements exist at all, it is highly probable that they occur only in small quantities, or in comparatively obscure places, otherwise they would have been discovered by one investigator or another using chemical, physical, or physical chemical methods.

There is, on the other hand, the probability that substances which we now regard as elementary, may prove to be compounds of still simpler substances. A substance is for us an element, which we have not been able thus far to break down into anything simpler. It is quite conceivable, however, that as old methods are improved and new ones devised, we may be able to effect decompositions not thus far accomplished. One would naturally turn in this connection to electrical methods, by means of which very high temperatures can be easily realized. Since, however, this is pure speculation, entirely unsubstantiated thus far by fact, it is not profitable to pursue it farther.

The Chemical Elements. — Having learned what is meant by the term "chemical element," we naturally ask which are the elements and what substances are compounds? In the following table the substances which have been shown with a reasonable degree of probability to be elementary, are given, together with the symbol which is used for the element in question: —

Aluminium	Al	Barium	Ba
Antimony	Sb	Bismuth	Bi
Argon	A	Boron	B
Arsenic	As	Bromine	Br

Cadmium	Cd	Nitrogen	N
Cæsium	Cs	Osmium	Os
Calcium	Ca	Oxygen	O
Carbon	C	Palladium	Pd
Cerium	Ce	Phosphorus	P
Chlorine	Cl	Platinum	Pt
Chromium	Cr	Potassium	K
Cobalt	Co	Proseodymium	Pr
Columbium	Cb	Rhodium	Rh
Copper	Cu	Rubidium	Rb
Erbium (?)	E	Ruthenium	Ru
Fluorine	F	Samarium	Sm
Gadolinium	G	Scandium	Sc
Gallium	Ga	Selenium	Se
Germanium	Ge	Silicon	Si
Glucinum	Gl	Silver	Ag
Gold	Au	Sodium	Na
Helium	He	Strontium	Sr
Hydrogen	H	Sulphur	S
Indium	In	Tantalum	Ta
Iodine	I	Tellurium	Te
Iridium	Ir	Thallium	Tl
Iron	Fe	Thorium	Th
Krypton	Kr	Thulium	Tu
Lanthanum	La	Tin	Sn
Lead	Pb	Titanium	Ti
Lithium	Li	Tungsten	W
Magnesium	Mg	Uranium	U
Manganese	Mn	Vanadium	V
Mercury	Hg	Xenon	X
Molybdenum	Mo	Ytterbium	Yb
Neodymium	Nd	Yttrium	Y
Neon	Ne	Zinc	Zn
Nickel	Ni	Zirconium	Zr

The symbol of the element is usually the first letter, or this combined with some other distinctive letter when several elements begin with the same letter. In some cases, however, the symbol is not taken from the English name of the element, but from the Latin. Thus, the symbol for copper is Cu, from the Latin *cuprum;* the symbol for iron Fe, from the Latin *ferrum;* etc.

Some elements occur in very large quantities in the earth, while

others are comparatively rare. The following estimate of the composition of that part of the earth which is accessible to us seems on the whole the most reliable:—

Oxygen, percentage in the earth	50.0
Silicon, " " " "	25.0
Aluminium, " " " "	7.2
Iron, " " " "	5.0
Calcium, " " " "	3.5
Magnesium, " " " "	2.5
Sodium, " " " "	2.3
Potassium, " " " "	2.2
Hydrogen, " " " "	1.0
Titanium, " " " "	0.3
Carbon, " " " "	0.2

The earth is thus made up chiefly of nine elements, the remainder occurring in comparatively small quantities.

Chemical Combination.—Certain elements can combine with certain other elements and form compounds. Two elements may combine and form a compound, or three, four, or more elements may combine. We may, therefore, have compounds containing two, or a much larger number of elementary substances. Most chemical compounds contain two or three elements, but some contain four, five, or six, or even a larger number of elements.

While elementary substances may combine with one another and form compounds, it is not true that any element can combine with any other element. We shall learn that elements with widely different properties generally combine most readily, while the elements whose properties are similar may not combine at all, or if they form compounds, these are often readily decomposed.

When elements combine and form a compound, this is expressed by writing the symbols of the elements with a plus sign between them on the left-hand side of the equality sign, and the symbols of the elements which enter into the compound on the right-hand side of the equation. Thus, when the elements hydrogen and oxygen combine to form water, this is expressed chemically as follows:—

$$H_2 + O = H_2O.$$

Such an expression is known as a *chemical equation*.

The science of chemistry consists, in part, of a study of the elements and the compounds which these elements can form with one another. Certain generalizations have been reached to which chemical reactions between substances conform. To these we shall now turn.

CHAPTER II

GENERALIZATIONS

The Science of Chemistry. — The study of chemical phenomena, like the study of phenomena in general, consisted at first in simple observation and description. Two substances were allowed to react chemically and the reaction was observed. The nature and properties of the substances entering into the reaction were studied, and then the nature and properties of the products formed. This was the qualitative stage of chemistry.

Mere qualitative observations are followed by quantitative measurements in the development of any branch of natural science. The mind is not content with merely observing phenomena at long range, as it were. It desires to study them in detail and quantitatively, and this marks the second stage in the development of a branch of science. The quantities of the substances which enter into a reaction were carefully weighed, and the quantities of the products formed. The amounts of different substances which combine with one another were determined, and certain other changes which take place simultaneously with chemical transformations were studied.

Just as the qualitative stage in the development of any branch of science leads to the discovery of a large number of facts, so the quantitative period brings to light an enormous mass of details which are placed upon record. Still we do not have a science. A heterogeneous mass of isolated facts, however large and however well established, is not a science. Indeed, the highest aim of a science is not simply to observe and record facts.

Facts bear about the same relation to a science as the bricks to a magnificent piece of architecture. They are absolutely essential to it, but they are only a means to an end.

Generalization. — The highest aim of scientific investigation is the discovery of wide-reaching relations between large numbers of facts. Such relations when sufficiently comprehensive are known as generalizations. Beyond these we cannot go. Whether they are absolute truths to which all phenomena conform we cannot say, because we cannot observe all the cases to which they apply. Take

a simple example by way of illustration. It was early observed that a body thrown upward from the surface of the earth will return again to the surface. Repeated observations confirmed those first made, but it remained for Newton to arrive at the generalization known as the law of gravitation.

In a similar manner certain generalizations have been reached in chemistry, which have been of fundamental importance in the development of the science. Some of these will be considered in this place, while others will be introduced in connections into which they seem to enter naturally.

The Law of the Conservation of Mass. — We have seen that when substances react chemically they disappear as such, and products are formed having properties very different from the original substances. When copper was heated in the air a black powder was formed having properties which are very different from the original copper. The question arises, are all the properties of the copper lost during the chemical transformation, or have only some of them disappeared? It is easy to convince ourselves that most of the properties of the copper have been lost during the reaction, but it is a very much more difficult problem to determine whether all the properties have disappeared. Take the property mass. Does the mass of the substances entering into a chemical reaction undergo any change during the reaction? This is a question very easy to raise but very difficult to answer with any high degree of accuracy.

Since weight is a measure of mass, the problem reduces itself to determining whether there is any change in weight under similar conditions when chemical reaction takes place? The weighings must be made under similar conditions, before and after the reaction, since the weight of any given substance is a function of the conditions, especially the distance from the centre of the earth — a body weighing more in a deep valley than on a high mountain.

We can answer this question then only to within the limit of accuracy of the most refined chemical balance, and some of the most accurate work in the whole field of chemistry has been done in connection with this problem.

It has been established for a comparatively long time that if there is any change in mass in chemical reaction it is very small. This, however, leaves entirely unanswered the question as to whether there might not be a *slight* change in mass when substances react chemically.

This question has recently been studied with a degree of accuracy which has rarely been approximated and never surpassed in the whole

history of chemical investigation. The German physical chemist, Landolt, of the University of Berlin, had constructed probably the most accurate chemical balance which has ever been made. With this he weighed the substances before the reaction and then weighed the products of the reaction. Although very slight differences in weight were detected, yet these were in no case greater than the possible experimental error. His work and subsequent investigations along the same line confirm the earlier conclusion that there is no appreciable change in weight, and, consequently, no appreciable change in mass in chemical reaction. This is known as the *law of the conservation of mass.*

The importance of this generalization for the science of chemistry cannot be easily overestimated. If mass did change in chemical reaction, it would be meaningless to work quantitatively where chemical transformations take place. The whole subject of quantitative analysis would be very different from what it is to-day, and an exact science of chemistry would be next to impossible.

The law of the conservation of mass is sometimes referred to as the law of the conservation of matter. The former expression is greatly to be preferred to the latter, since it states just what has been established by experiment. The latter is pure theory, having no known connection with fact.

The Law of Constant Proportion. — The second important generalization which was reached through the quantitative study of chemical phenomena, was that the constituents of a chemical compound are always present in a constant proportion. If two substances react chemically and form a third, they enter into combination in a constant proportion. The law may be formulated thus: —

Any given chemical compound always contains the same constituents, and there is a constant proportion between the masses of the constituents present.

The law of constant proportions was called in question in the early years of the nineteenth century by the French chemist, Berthollet, in his great book, *Essai de statique chimique.* Berthollet was deeply impressed by the effect of the quantity of substance used on the nature of the chemical reaction, and saw in outline what we shall learn to be one of the most important laws of chemical activity. He thought that not only the nature and magnitude of the reaction were affected by the masses of the substances used, but also the composition of the products formed. Two substances could unite in a great many proportions, and the composition of the product de-

pended chiefly on the relation between the amounts of the substances used.

The error of Berthollet was corrected by Proust, who showed that many of the substances which Berthollet had supposed to be compounds were mixtures of different substances. This, however, is not a severe reproach to Berthollet, since the methods for effecting separations and analyzing substances were very crude indeed, at his time, and it arouses our deep admiration when we consider what was accomplished under the conditions which then prevailed.

Subsequent work with the more refined methods has shown that the law of constant proportion is a fundamental law of chemistry. We should mention especially the classical work of the Belgian, Stas. He tested this law with a thoroughness and accuracy which have rarely been equalled in any branch of science. The result is what has already been indicated. The law has stood the most refined and crucial experimental test.

The Law of Multiple Proportions. — While it is true that substances combine in constant proportions, it is also true that two substances may combine in more than one proportion. The two compounds methane and ethylene were analyzed, and it was found that the ratio of carbon to hydrogen in the former was as 3 to 1; in the latter as 6 to 1. The latter evidently contains twice as much carbon with respect to hydrogen as the former. A number of analogous cases where two elements combine in more than one proportion were examined, and the result was the discovery by Dalton of the law of multiple proportions. This law may be formulated thus: —

If two elements combine in more than one proportion, the masses of the one which combine with a given mass of the other bear a simple, rational relation to one another.

Since this law was proposed, great masses of facts which bear upon it have been discovered. The result is that the law has been found to hold thus far without an exception.

The importance of the law of multiple proportions for the science of chemistry is very great. If this law did not govern chemical reactions, the number of compounds which any two elements might form with one another would be very great. As it is, any two elements can form only a limited, and usually a comparatively small, number of compounds with each other.

One further point should be mentioned in connection with this

law. It shows that chemical reactions proceed by steps or leaps, as it were. One part of A combines with one of B, or with two of B, or with three of B; not one part of A with one and a fraction of B, or two and a fraction of B. The importance of this fact as bearing upon the possibility of an exact science of chemistry is very great indeed. While it is impossible to see its significance at this stage of our subject, it may be stated that it is this law more than any other which, for a long time, made it difficult to apply mathematics to chemical phenomena. These breaks, or lack of continuity, made it extremely difficult to use the calculus in dealing with chemical phenomena as it could be used in dealing with the phenomena of physics, and are the most potent reason why chemistry has developed so much more slowly than physics, and is still, strictly speaking, not an exact science.

The Law of Combining Weights. — There is a third law to which the masses of substances which combine with one another conform. If we determine the weights of different substances which combine with a given weight of a definite substance, these weights, or simple multiples of them, represent the quantities of the different substances which will combine with one another. Thus, 35.45 parts of chlorine combine with 1 part of hydrogen, and 79.96 parts of bromine combine with 1 part of hydrogen. When chlorine and bromine combine, 35.45 parts of chlorine combine with 79.96 parts of bromine. Again, 40.1 parts of calcium combine with 16 parts of oxygen, and 65.4 parts of zinc combine with 16 parts of oxygen. If calcium and zinc combined, 40.1 parts of calcium would combine with 65.4 parts of zinc.

The quantities of substances which combine with one another have been termed their combining numbers or combining weights, and the law is known as the law of combining weights. The law may be stated thus: —

Substances combine either in the ratio of their combining numbers, or in simple, rational multiples of these numbers.

Of all the elements, hydrogen combines with other elements in smaller quantity by weight than any other element. Its combining number, being the least of all the elements, is taken as unity. We shall become familiar with the combining weights of the elements in another connection. Suffice it to say here that this law, like the laws of constant and multiple proportions, has been subjected to the most careful experimental test, and has been shown to be true to within the limit of error of some of the most refined experimental work.

The Atomic Theory.—The discovery of empirical relations such as the three laws of chemical combination just considered, is of great importance, and is absolutely essential to scientific progress; but these are of interest chiefly as they lead to correct theories and wide-reaching generalizations. Dalton raised the question, What do the laws of definite and multiple proportions really mean? Why do such relations obtain? His answer is what has come to be known as the scientific atomic theory, in contradistinction to the older imaginative speculations about atoms and molecules. The view that matter is composed of indivisible particles or atoms, which have definite weights, and that chemical action takes place between these particles, was to Dalton the only rational explanation of the laws of multiple proportion and combining weights. If water is composed of such ultimate, indivisible parts or atoms, then a constant number of atoms of one substance combines with one atom of another substance to form a definite *molecule* of the compound, and we have the law of constant proportions. One atom of one substance may combine with one atom of another substance, or a number of atoms of one substance may combine with one of another to form a molecule, but the number must be a simple, rational, whole number; whence the law of multiple proportions.

Since the atoms have definite weights, and the laws of constant and multiple proportions are true, the law of combining numbers follows as a necessary consequence of the atomic theory.

The question as to the *size or mass of an atom* is one which is still open to some doubt. We know that they are inconceivably small. This is shown by the fact that certain substances will continue to give off odors for a long time, which fill a large space, and still not lose appreciably in weight. The odoriferous particles must be present in every part of the space, and although the substance will continue to fill this space with such particles for months or longer, the amount of matter which has volatilized is scarcely weighable. This shows the almost unlimited divisibility of which matter is capable, and by definition the atom is indivisible. The same fact is brought out by dissolving certain coloring matters such as the aniline dyes in water. Very small amounts of such substances can impart an appreciable color to comparatively enormous volumes of water. The coloring matter must be capable of almost unlimited divisibility in order that this may be effected.

Perhaps, on the whole, the best idea of the size of atoms has been furnished us by Lord Kelvin in England. In his own words: "Imagine a raindrop or a globe of glass as large as a pea, to be mag-

nified up to the size of the earth; each constituent being magnified in the same proportion. The magnified structure would be coarser-grained than a heap of small shot, but probably less coarse-grained than a heap of cricket balls."

The Correlation and Conservation of Energy. — We have been considering thus far entirely the material transformations which take place in chemical reactions, and have pointed out certain generalizations which have been reached, and which lie at the foundation of the science of chemistry. Were we to stop here and begin our study of the several elements, we would leave untouched a class of phenomena whose importance cannot easily be overestimated.

Whenever we have chemical reaction taking place we have heat liberated or absorbed, and usually liberated. This brings us to a study of the energy changes which are inseparably connected with all chemical action.

Energy manifests itself in a number of forms. We have light energy, heat energy, electrical energy, mechanical energy, and these are mutually convertible into one another. That mechanical energy can be converted into heat is shown wherever friction exists. Rub together two pieces of metal and both become hot. That heat energy can be converted into light energy is illustrated by a piece of metal which has been heated to incandescence. That heat energy can be converted indirectly into electrical energy is shown by the dynamo, and so on. This principle of the mutual convertibility of the various forms of energy is known as the *principle of the correlation of energy,* and is an important generalization in physical science.

That one form of energy can be converted *qualitatively* into another is important, but far less important than the fact that one form of energy can be converted *quantitatively* into another. When, for example, mechanical energy disappears, as when a hammer falls upon a metal plate, the heat energy produced is exactly equivalent to the mechanical energy which has disappeared. If the heat energy produced under these conditions was transformed into work, it would raise the hammer again exactly to its original position. This principle, fundamental to the science of physics, is known as the *principle of the conservation of energy.* It says in words that no energy can be created or lost, and is analogous to the law of the conservation of mass, which we have already studied.

Importance of the Conservation of Energy for the Science of Chemistry. — The bearing of the conservation of energy upon chemistry may not appear at first sight. In addition to the forms of

energy enumerated above we should add intrinsic energy, which is frequently referred to as chemical energy. This form of energy exists in practically all substances in larger or smaller amounts, and is the form which is converted into heat when a piece of coal is burned. The existence of this form of energy is essential to all chemical action, and is, therefore, absolutely essential to the science of chemistry. It is this form of energy which is converted into heat whenever a chemical reaction takes place with the evolution of heat. Indeed, the transformation of intrinsic energy into heat lies right at the foundation of most chemical reactions and is the chief cause why such reactions take place. It is sometimes stated that chemical reactions are accompanied by heat evolution. This statement is misleading, since it lays stress upon the less important phenomenon. Indeed, it confuses cause and effect. We should probably be much nearer the truth if we said that the thermal change was accompanied by material transformations, which gave rise to new products with properties for the most part different from those of the original substances.

Although we cannot discuss this point more fully in the present connection, we can see that the energy changes which take place during chemical reaction are of prime importance.

Although only a part of the intrinsic or chemical energy in the substances which react is converted into heat or some other form of energy during the reaction, yet this part which disappears is converted quantitatively into other forms. The law of the conservation of energy is, therefore, fundamental to the scientific study of chemistry.

CHAPTER III

OXYGEN (At. Wt. = 16.0)

Occurrence in Nature. — Oxygen is the most abundant of all the chemical elements. It forms about 88.8 per cent of all the water on the earth, and about 23 per cent of the atmospheric air. It is an important constituent of most of the rocks, and occurs in nearly all living matter whether vegetable or animal. It is estimated in general that about one-half of the earth's crust is composed of the element oxygen.

Preparation of Oxygen. — Since oxygen occurs in such large quantities in nature, we would think that we should turn to some natural source for a supply of this element. It is, however, not very easy to obtain pure oxygen from any natural source. It can be obtained from the air, but not very readily. It is much more difficult to separate it from its compounds in the rocks. It can be obtained from water by decomposing the water by means of an electric current, but there are far more economical and convenient means of preparing oxygen than by the electrolysis of water.

One of the most convenient means of obtaining oxygen in the laboratory is by *heating potassium chlorate.* This compound, which is represented by the formula $KClO_3$, contains about 39 per cent of oxygen, and gives up all of its oxygen when moderately heated. The decomposition of the chlorate proceeds in two distinct stages, which we shall study later in more detail. The final result is as indicated; all the oxygen is set free and potassium chloride remains behind. This is expressed by the following equation: —

$$2\,KClO_3 = 2\,KCl + 3\,O_2.$$

Another method of preparing oxygen is by *heating mercuric oxide.* It is decomposed at once into metallic mercury and oxygen in the sense of the following equation: —

$$2\,HgO = 2\,Hg + O_2.$$

Hydrogen dioxide, a compound having the composition expressed by the formula H_2O_2, when brought in contact with many substances

such as the metals, or compounds which are themselves rich in oxygen, gives up half of its oxygen, becoming water: —

$$2\,H_2O_2 = 2\,H_2O + O_2.$$

Oxygen can be readily obtained from the compound *barium dioxide.* When ordinary barium oxide, BaO, is heated and a current of air passed over it, it takes up oxygen from the air, becoming barium dioxide. When the dioxide is subjected to diminished pressure, it gives off oxygen and passes back again into barium oxide.

$$2\,BaO_2 = 2\,BaO + O_2.$$

This is the most convenient means of obtaining oxygen from the air in pure condition. The oxide of barium takes up oxygen from the air, forming the dioxide of barium, which can in turn be decomposed into oxygen and oxide of barium. The latter can be converted again into the dioxide and the process continued at will.

Substances burn readily in Oxygen. — One of the most characteristic of the chemical properties of oxygen is the readiness with which substances burn in it. Substances which burn comparatively slowly, or will not burn at all in the air, often burn with the greatest readiness in oxygen gas, emitting very bright light and evolving large quantities of heat.

Fill a number of glass vessels with oxygen gas in the following manner: First, fill the vessels with water and invert them in a trough containing water. Place some potassium chlorate in a glass retort, connect a piece of rubber tubing with the neck of the retort, and then heat the retort gently with a Bunsen burner. After all the air has been expelled, bring the end of the rubber tube beneath the mouth of the glass vessel and continue to heat the retort. The oxygen which is set free by the decomposing potassium chlorate will rise in the glass vessel and displace the water with which it is filled.

The arrangement of the apparatus for preparing oxygen is shown in Fig. 1. The glass retort *R* containing the potassium chlorate is heated by the Bunsen burner *B*. The glass cylinder *C* is filled with water and dips beneath the water in the glass trough *T*. The rubber tube *A* is placed beneath the mouth of the glass cylinder after all the air has been expelled from the retort, and the cylinder filled with oxygen gas. Fill a number of such cylinders with oxygen gas and the following experiments can be readily carried out.

Ignite a pine splinter until it burns to a coal. Extinguish the flame and plunge the splinter with the coal on the end into a vessel containing oxygen. The splinter will burst again into flame.

Place a piece of sulphur in a deflagrating spoon of convenient shape and size; ignite the sulphur and plunge it into a vessel filled with oxygen. The sulphur, which in the air burns with a blue flame of small luminescence, bursts into violent combustion in the oxygen, evolving large amounts of heat and light.

A piece of carbon is placed in a similar spoon heated to redness, and plunged into a vessel filled with oxygen. The carbon burns vigorously, with evolution of large amounts of heat and light.

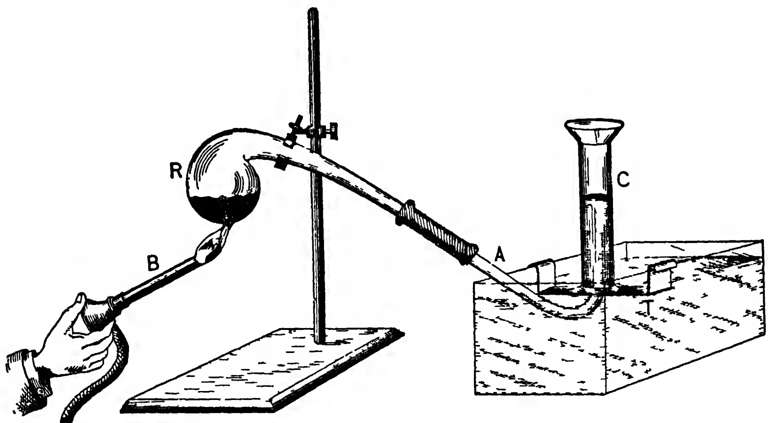


FIG. 1.

While a piece of iron will not burn with any appreciable velocity in the air, it burns very readily indeed in pure oxygen. This can be shown as follows: Take a steel watch-spring and wrap one end with cotton thread. Plunge this end into molten sulphur, when a comparatively large amount of the sulphur will adhere to the thread. Ignite the sulphur and then plunge the iron into the vessel of oxygen. The sulphur will first burn vigorously and heat the iron to a very high temperature. The iron will then burn in the oxygen with an intense white light, and a large number of highly heated particles will fly off from the iron, producing quite a pyrotechnic effect. In this experiment it is well to have the vessel containing the oxygen placed upon a stone slab or immersed in a vessel containing water, since otherwise the molten iron may fall upon the support to the vessel and break it, thus interrupting the experiment. This experiment illustrates particularly well the difference between combustion in the air and in oxygen.

Another experiment which is frequently used to illustrate this same point is the burning of phosphorus in air and in oxygen. While

phosphorus burns quietly in the air, in pure oxygen the combustion takes place with great violence. Introduce a small piece of phosphorus into a deflagrating spoon, ignite it, and immerse it in a vessel filled with oxygen. The vessel should be large to avoid being broken by the heat which is liberated in such large quantities. It is also advisable to take the precaution to wrap the vessel with a towel, to avoid pieces of glass from flying in case the vessel should break.

Explanation of the Above Results. — The above results show beyond question that certain substances which burn slowly in the air, or do not burn at all, burn readily in pure oxygen. This naturally raises the question why this is the case. The air, as we shall learn, is essentially oxygen diluted with about four times its volume of nitrogen. The number of oxygen particles in a given volume of air is, therefore, much less than in a given volume of pure oxygen. The nitrogen serves to dilute the oxygen. When combustion takes place in pure oxygen, the heat which is liberated is expended in raising the temperature of the oxygen alone, and the rapidity of the combustion depends chiefly upon the temperature of the oxygen gas.

When the oxygen is diluted with an inert gas like nitrogen, much of the heat which is set free during the combustion is expended in raising the temperature of the nitrogen, which takes no part in the combustion, and as far as accelerating the combustion is concerned is, therefore, lost.

COMBUSTION

Combustion. — The subject of combustion, or burning, is one which has attracted the attention of chemists from very early times. This would be expected, since combustion is among the most familiar of chemical phenomena. There is evidence that fire was known very early in the development of the human race, and its economic importance cannot of course be easily overestimated. When combustion was first observed, chemical knowledge, if such it may be called, was of the very crudest sort. The conception of elements did not exist, still less the conception of the element oxygen. They observed that substances apparently disappeared either wholly or in part when burned, and they saw the fire or flame escape from the burning mass.

The Phlogiston Theory of Combustion. — The tendency of the human mind in time past was the same in one respect as it is to-day. It was not content with simply observing facts; it wished to account for them and explain them, hence the origin of theories. From all the facts which were early observed concerning combustion, especially the disappearance of the substances as they burned and the escape

of flame, it seemed evident that in combustion something escaped. Although they could not discover what this substance was they applied a name to it. It was termed *phlogiston,* and the theory, *the phlogiston theory of combustion.*

According to this theory when a substance burned it gave off phlogiston, and the products of combustion differed from the substance before it was burned in that they had lost phlogiston.

This theory of combustion held sway until oxygen was discovered by Priestley and Scheele about 1774–1775. The study of oxygen and the part it played in combustion entirely overthrew the phlogiston theory of combustion.

The Rôle of Oxygen in Combustion. — It was shown by the Swedish chemist Scheele, that atmospheric air in which a substance has been burning for a time is no longer able to support combustion. This made it probable that there was something in the air which had disappeared during combustion. Scheele and also Priestley showed how a gas could be obtained which supported combustion far better than atmospheric air. The former obtained his gas by heating saltpetre, the latter by heating oxide of mercury.

It remained, however, for the French chemist Lavoisier to show the real significance of oxygen in all ordinary cases of combustion. When a substance burned it united with oxygen, and combustion consists in the union of the substance burned with oxygen. This is the conception of combustion which we hold at the present day, and is diametrically opposed to the theory of phlogiston. According to the phlogiston theory of combustion something escapes when a substance is burned; according to the present theory an element, oxygen, is added to the substance which is undergoing combustion.

Increase in Weight in Combustion. — If combustion consists in the union of oxygen with the substance burned, then the weight of the products of combustion must be greater than the weight of the substance which has been burned. This alone would seem to be a crucial experiment to decide between the phlogiston theory and the oxygen addition theory of combustion. It would only be necessary to weigh the body which is to be burned, and to weigh the products of combustion, and see which is the heavier.

The phlogistonists, however, would not admit that this was any test of their theory. Indeed, in the later period of the theory they knew very well that the products of combustion are heavier than the substance before it was burned. This fact they easily reconciled to their theory. They said that phlogiston has negative weight — weighs less than nothing — and when it escapes from a substance as

in combustion, the substance becomes heavier. This line of argument would hardly appeal to any one at the present day, and is given simply on account of its historical interest.

That the products of combustion weigh more than the substance before it was burned can be readily shown by the following experiment (Fig. 2): Two pieces of candle of equal length are placed, one upon each pan of a large balance. A lamp chimney is suspended from each end of the arm of the balance. A piece of wire gauze which fits the chimney tightly is introduced into each chimney, and some coarse pieces of caustic soda added. Caustic soda is now added to the lighter side until the pointer stands exactly in the middle of the scale.

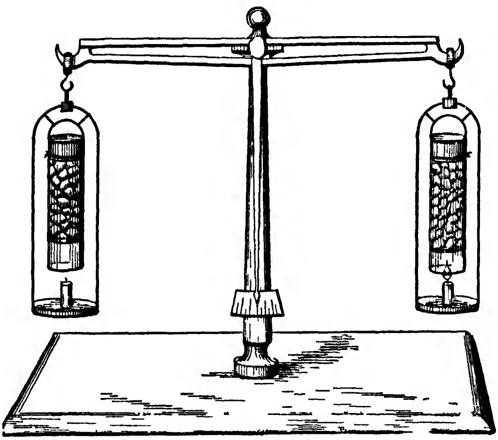


Fig. 2.

One of the candles is now lighted, and the products of the combustion, carbon dioxide and water, are caught by the caustic soda. After the candle has burned for a time this arm of the balance will begin to sink, showing that the products of combustion of the candle are heavier than the unburned candle.

Oxygen used up in Combustion. — That oxygen is actually used up in combustion can be readily shown by the following experiment. Fill a glass tube with air as shown in Fig. 3. Introduce a piece of phosphorus. This will undergo slow combustion and the oxygen will be used up, as is shown by the fact that the water will rise steadily in the tube.

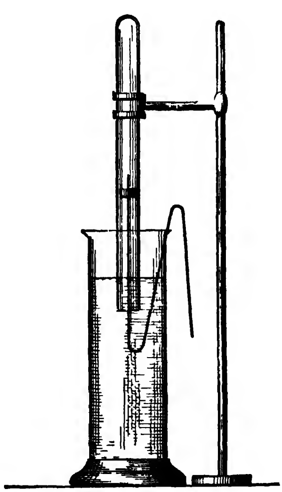


Fig. 3.

Experiment 2 shows that the products of combustion are heavier than the substance before it is burned, and experiment 3 that oxygen is used up in combustion. It is oxygen

which adds itself to the burning substance, and combustion is nothing but oxidation.

Rapid and Slow Oxidation.—Combustion, as we ordinarily observe it, is a comparatively rapid process. The substance burns up, as we say, in a few minutes, and there is usually a large evolution of heat, and in many cases a marked production of light. This is known as rapid oxidation.

We know oxidation processes, however, which take place slowly and extend over long periods of time, even years. Examples are the oxidation of metals, the decaying or slow oxidation of wood, and the like.

When the oxidation proceeds slowly, as in these cases, there is no apparent evolution of heat and no evolution of light. The question arises, Are we justified in concluding that there is actually no evolution of heat when slow oxidation takes place? We cannot detect any heat set free, but it might readily be that there is a slow evolution of heat, but so slow that it escapes before it can be detected.

While we cannot prove directly, unless large masses of substances are employed, that heat is set free in slow oxidation, it can be proved indirectly. The products of slow oxidation are in many cases the same as the products of rapid oxidation where much heat is evolved. Since the original substances which combine are the same whether the oxidation is slow or rapid, and since the products are the same, the same energy relations obtain whether the oxidation is rapid or slow. From the conservation of energy, then, we know that heat is evolved in slow oxidation as well as in rapid oxidation, and further, that exactly the same amount of heat is evolved when a given quantity of any substance is oxidized to a given oxide, whether the oxidation takes place slowly or proceeds rapidly to the end. This necessary consequence of the law of the conservation of energy is of more than ordinary interest.

Measurement of the Heat of Combustion.—The measurement of the amount of heat which is set free when combustion takes place is not a simple operation. Indeed, the accurate measurement of the amount of heat is always more or less difficult, on account of the fact that heat always flows from the warmer to the colder body, and so many substances are comparatively good conductors of heat.

To measure the amount of heat set free in any chemical reaction, such as combustion, the reaction must be carried out in a vessel surrounded by a poor conductor of heat, so that the loss in heat will be reduced to a minimum. The heat which is produced is allowed to warm a known weight of water, and the temperature of the water

is noted before and after the experiment. The apparatus which is used for measuring quantity of heat is known as a calorimeter. It consists of an innermost vessel into which a weighed amount of water is introduced. The reaction takes place in this vessel or in a vessel which is immersed in the water. The vessel containing the water is surrounded by some poor conductor of heat, such as felt or eider-down. This is then surrounded by one or two layers of air, which is a poor conductor of heat. Even when all of these precautions are taken to prevent loss of heat, the rate at which the calorimeter loses heat must be determined, and a corresponding correction introduced. If we know the amount of water used in the calorimeter and the rise in temperature produced, we know the amount of heat set free as the result of the reaction.

Some unit must be adopted for expressing the results of calorimetric measurements. Whatever unit we select would be purely arbitrary. The amount of heat which is required to raise one gram of water one degree in temperature has been proposed as the unit of quantity of heat. Since this quantity depends upon the temperature of the water, and varies quite appreciably with the temperature, it is necessary to define the temperature. The amount of heat required to raise one gram of water from 0° to 1° C. is taken as the unit, and is called the *calorie*, and written *cal.* The calorie is sometimes defined as one one-hundredth of the amount of heat required to raise one gram of water from zero to one hundred degrees. The two definitions are for all practical purposes essentially the same.

Sometimes it is more convenient to use a larger unit, and two such have been proposed and adopted. One is one hundred times the smaller calorie, and is written *Kal.* The other is one thousand times the smaller calorie, and is written *Cal.* The relations which exist between the three units is, then, 1 $Cal = 10\ Kal = 1000\ cal.$

In order that the heats of combustion of substances may be comparable, we must use comparable quantities. We might take any arbitrary quantity of different substances, say ten grams of each. But these quantities would not be comparable, since they would not represent the quantities of the different substances which would combine with one another. It is best to take quantities of the different substances which are proportional to their combining weights, but more of this later.

Heat of Formation and of Decomposition.—We have just seen that when two or more substances unite and form a third substance, heat is evolved. Further, a definite amount of heat is

set free when a given amount of any substance is formed. This amount is known as the heat of formation of the substance.

Given a substance already formed by the union of two or more substances. A certain amount of heat must be added to it to decompose it into its elements. This is known as the heat of decomposition of the substance.

A very beautiful relation has been established between the heat of formation of a substance and its heat of decomposition. *The two are equal.* This will be seen at once to be a necessary consequence of the law of the conservation of energy. Starting with any substances, we allow them to combine. If now we decompose the compound formed into the original substances, we come back to exactly the same condition under which we started, and the same energy relations must obtain at the end as at the beginning of the process. Exactly the same amount of heat which was set free during the formation of the compound must be added to the compound to decompose it again into its elements.

Names of the Compounds formed with Oxygen. — The compounds of oxygen with the other elements are termed *oxides*. When sulphur was burned in oxygen, the gaseous compound formed is known as oxide of sulphur. The name actually used, however, is even more explicit. One atom of sulphur combines with two atoms of oxygen, giving the compound SO_2. To indicate the presence of two oxygen atoms in the molecule the compound is termed sulphur dioxide.

The compound formed when carbon burns in oxygen is known as oxide of carbon. There are, however, two oxides of carbon, one containing one atom of oxygen to one of carbon (CO), and the other, two atoms of oxygen to one of carbon (CO_2). The one formed in our earlier experiment, where carbon was burned in pure oxygen, contains two atoms of oxygen to one of carbon and is known as carbon dioxide. The oxide of carbon containing one atom of oxygen to one of carbon is known as carbon monoxide.

When phosphorus is burned in pure oxygen, the resulting compound has the composition represented by the formula P_2O_5. This is known as the pentoxide of phosphorus. There is another oxide of phosphorus having the composition P_2O_3, and this is known as the trioxide of phosphorus.

When iron is burned in oxygen the resulting compound has the composition Fe_3O_4 and is known as ferrous ferric oxide, while the compound FeO would be known as ferrous oxide. The compound Fe_2O_3 is ferric oxide. The terms "ic" and "ous" have come to have

a generic significance; "ic" is applied to the oxide richer in oxygen, and "ous" to the oxide which contains less oxygen.

PHYSICAL PROPERTIES OF OXYGEN

Certain Physical Properties of the Element Oxygen. — Oxygen under ordinary conditions is a transparent, colorless, odorless gas. It is somewhat heavier than air, having a specific gravity in terms of air as unity of 1.1056. A litre of oxygen under normal conditions of temperature and pressure, *i.e.* at 0° and 760 millimetres pressure, weighs 1.4296 grams. In terms of hydrogen as the unit the specific gravity of oxygen is 15.88. This we shall learn is the ratio between the relative weights of the atom of hydrogen and the atom of oxygen. Oxygen is only slightly soluble in water. At 0° 100 volumes of water dissolve 4 volumes of oxygen. At 15°, 100 volumes of water dissolve 3.4 volumes of oxygen. Oxygen is much more soluble in alcohol than in water, 100 volumes of alcohol dissolving about 28 volumes of oxygen.

The Pressure of Oxygen varies with the Conditions. — We have referred to the weight of a litre of oxygen under normal conditions of temperature and pressure. This would imply that the weight of a litre of oxygen would change if we changed temperature or pressure, and such is the fact. If we have a litre of oxygen at any given pressure and subject the gas to a greater pressure, the volume would be less than a litre, and, consequently, the density of the gas would be increased and the weight of a given volume of the gas increased. Similarly, diminution in pressure would cause increase in volume, and, consequently, diminution in the weight of a given volume of the gas.

If instead of varying the pressure we vary the temperature to which the oxygen gas is subjected, we would also produce change in volume. If the temperature of the gas is increased and the pressure kept constant, the volume of the gas would increase. If, on the other hand, the temperature of the gas is lowered, the pressure being kept constant, the volume of the gas would be diminished. Certain quantitative relations between the pressure and volume, and the temperature and volume of not only oxygen gas, but of gases in general, have been established, and these will now be briefly considered.

The Law of Boyle for Gases. — As already stated, the volume of a gas becomes smaller with increase in pressure, and with increase in pressure the density of a gas becomes greater. The relation connecting these properties is very simple. The pressure of a gas is

proportional to its density, and both are inversely proportional to the volume. If we represent the pressure by p and the density by d, we have —

$$p = cd,$$

where c is a constant for a given temperature. If v is the volume and m the mass of the gas, Boyle's law may be expressed thus: —

$$pv = cm.$$

If p is the pressure and v the volume of a given mass of gas under one set of conditions, and p_1 and v_1 the pressure and volume of the same mass of gas under other conditions, Boyle's law may be expressed thus: —

$$pv = p_1v_1.$$

The product of the pressure and volume of a given mass of gas at constant temperature is a constant.

While there are many exceptions known to the law of Boyle, especially when the gas is under either very slight or very great pressure, it holds approximately in the great majority of cases, and is one of the two fundamental laws of gas-pressure.

The Law of Gay-Lussac for Gases. — If a gas is kept under constant pressure and its temperature raised, the volume will increase. If the volume is kept constant as the temperature rises, the pressure will increase. The remarkable fact has been discovered that the increase in the volume of the gas for a given rise in temperature is a constant, independent of the nature of the gas. All gases increase about $\frac{1}{273}$ (= 0.003665) of their volume at 0° C., for every rise of one degree in temperature. Gay-Lussac's law states that this temperature coefficient is constant for all gases.

If we keep the volume constant and warm the gas to t^0, the pressure P at this temperature is calculated from the pressure p_0 at 0^0 as follows: —

$$P = p_0\,(1 + 0.003665\,t).$$

If, on the other hand, the pressure is kept constant and the volume allowed to increase with rise in temperature, the volume at t^0, V, is calculated from the volume at 0^0, v_0, as follows: —

$$V = v_0\,(1 + 0.003665\,t).$$

If both pressure and volume are allowed to change when the gas is heated, the pressure and volume at t^0, p and v, are calculated from the pressure and volume at 0^0 as follows: —

$$pv = p_0v_0\,(1 + 0.003665\,t),$$

from which,
$$v_0 = \frac{pv}{p_0\,(1 + 0.003665\,t)}.$$

This is the expression generally employed for reducing a gas to what are termed normal conditions. If the volume v of the gas is read at a given pressure p and temperature t, we can calculate at once the volume at 0^0, v_0, and normal pressure p_0, which is taken as 760 millimetres of mercury. Exceptions are known to the law of Gay-Lussac as to the law of Boyle, but we have here a law which applies to gases in general.

The Determination of the Absolute Zero of Temperature. — The value of the constant 0.003665 is determined either by keeping the pressure constant and measuring the increase in volume with rise in temperature, or by keeping the volume constant and measuring the increase in pressure as the temperature rises. The values found by the two methods differ only slightly, and we take 0.003665 as very nearly the true value of the temperature coefficient of a gas.

This is very nearly $\frac{1}{273}$, which means that if a gas is cooled down to $-273°$ C., its volume would become zero if the law of Gay-Lussac held down to the limit. This temperature, termed the *absolute zero*, has now been nearly realized experimentally. It is quite certain that temperatures have been produced which are within twenty degrees of this temperature, as we shall see. It is, however, very probable that the laws of gas-pressure do not hold at these extremely low temperatures.

The Combined Expression of the Laws of Boyle and Gay-Lussac. — These two fundamental laws of gas-pressure can be combined in one expression.

If we represent temperature as measured from the absolute zero by T, the combined expression of the laws of Boyle and Gay-Lussac is: —

$$pv = \frac{p_0 v_0}{273} T.$$

$\frac{p_0 v_0}{273}$ is usually represented by R, when the above expression becomes,

$$pv = RT.$$

The Liquefaction of Oxygen. — Although oxygen is a gas under atmospheric pressure and at all ordinary temperatures, it does not follow that it is a gas at all temperatures and pressures. If we look into the history of the liquefaction of gases, we find, however, that oxygen resisted for a long time all efforts to liquefy it, and was placed among the so-called permanent gases.

The early work on the liquefaction of gases made it obvious that two conditions were necessary in order that a gas may be liquefied. It must be subjected to a high pressure and to a low

temperature. By fulfilling these conditions the English physicist Faraday was able to liquefy many of the more common gases There were several, however, which resisted all efforts to liquefy them, and among these was oxygen. Natterer subjected oxygen to a pressure of between 3000 and 4000 atmospheres, at the same time cooling it far below the ordinary temperatures, but was not able to obtain it in the liquid form.

It is quite certain that oxygen would have been known only in the gaseous state for a much longer period of time, had not the discovery been made which we owe to Andrews. He pointed out that there is a temperature above which a gas cannot be liquefied no matter how great the pressure to which it is subjected. This temperature he called the *critical temperature*, and for oxygen this is now known to be $-119°$.

This explains why Natterer was unable to liquefy oxygen when he subjected it to a pressure of more than 3000 atmospheres. The gas was not sufficiently cooled. It was above its critical temperature.

When oxygen was cooled down to its critical temperature, the pressure required to liquefy it was only 50 atmospheres, and this is known as the *critical pressure* of oxygen.

Oxygen was first liquefied in 1877, simultaneously by two experimenters, Pictet and Cailletet. The method of Pictet is based upon the fact that when a low-boiling liquid evaporates, especially when under diminished pressure, a temperature much lower than its own boiling-point is produced. By surrounding oxygen with liquid carbon dioxide which boils at $-78°$, and allowing the liquid to evaporate under low pressure, a temperature is produced ($-140°$) which is below the critical temperature of oxygen. At this temperature the oxygen liquefies at a pressure below its critical pressure.

The method of Cailletet is based upon a different principle. When a gas is strongly compressed and then suddenly allowed to expand, it cools itself enormously. Cailletet subjected oxygen to a pressure of about 300 atmospheres and then allowed it to expand suddenly. Drops of liquid oxygen were obtained.

A method of obtaining liquid oxygen in quantity, which is greatly to be preferred to either of the above, is that of Linde, who has done so much toward the liquefaction of the more resistant gases. The method is based upon the cooling of a strongly compressed gas on expanding. Air is compressed, then allowed to cool itself by expanding. This is made to cool another quantity of compressed air, which in turn

is allowed to expand and establish a still lower temperature. This colder air is then allowed to cool still another portion of compressed air, and so on until a temperature is reached at which air liquefies.

We have seen, however, that air is a mixture chiefly of oxygen and nitrogen. It now remains to separate the liquid oxygen from the liquid nitrogen. Nitrogen, as we shall learn, boils lower than oxygen. When a mixture of liquid oxygen and liquid nitrogen is exposed to ordinary temperatures, the nitrogen, being the lower boiling liquid, will boil off first, and finally leaves behind comparatively pure liquid oxygen.

This is a method of obtaining oxygen from the air in comparative purity and in enormous quantities, wherever a liquid air plant is available. It should be added to the methods discussed at the beginning of this chapter for obtaining oxygen.

Properties of Liquid Oxygen. — We owe our knowledge of the properties of liquid oxygen almost entirely to the Russians, Wroblewski and Olszewski, and to the Englishman, Dewar.

Wroblewski and Olszewski have contributed much to our knowledge of the element oxygen when in the liquid condition. Dewar, having at his disposal for liquefying gases the enormous plant of the Royal Institution of Great Britain, has obtained oxygen and other low-boiling liquids, as we shall see, in quantities never approached by any one else. Dewar has devised a form of apparatus for preserving liquid oxygen and other low-boiling liquids, which deserves special notice.

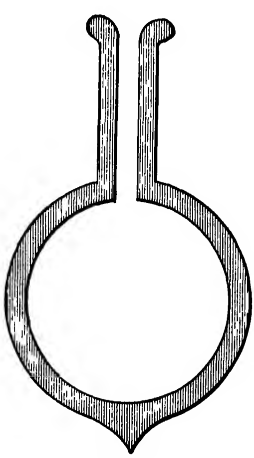


Fig. 4.

It is well known that a vacuum is a very poor conductor of heat. The rate at which a liquid will evaporate depends primarily upon the rate at which it can secure heat, which is absolutely necessary in order that the liquid may pass over into vapor. Dewar constructed double-walled, glass vessels and pumped out the air between the walls. The arrangement is shown in Fig. 4. The air is pumped out from the space between the two walls, and then the connection with the pump sealed off.

Liquid oxygen placed in such a "vacuum-jacketed" apparatus will evaporate comparatively slowly, and can be preserved for quite a time. Such forms of apparatus have greatly facilitated the study of low-boiling liquids.

Liquid oxygen is light blue in color, boils at $-181°$, and at its boiling-point has a specific gravity of 1.135, water being taken as the unit. The specific gravity varies so greatly with the temperature that at the critical temperature of oxygen, $-119°$, it is only 0.65.

It is obvious that liquid oxygen furnishes us with an excellent means of obtaining very low temperatures. While under atmospheric pressure it boils at $-181°$, when allowed to boil under a pressure of a few millimetres of mercury a temperature as low as $-225°$ can be obtained.

Power of Oxygen to enter into Chemical Combination. — The element oxygen has rather remarkable power of entering into combination with other elements. It combines with all of the more common elements with the exception of fluorine. Of the rarer elements it forms compounds with all except those recently discovered by Ramsay. These elements, argon, helium, neon, krypton, and xenon, do not combine with oxygen, but it should be said that thus far they have not been made to combine with any other substance or with one another. No chemical element combines more generally with other elements than the element oxygen.

OZONE

Allotropic Modification of Oxygen. — We have dealt thus far with the element oxygen in the condition in which it is ordinarily known to us. Oxygen can, however, occur with very different properties from ordinary oxygen. The second modification of oxygen is known as ozone. The property of an element to occur in two different modifications is known as *allotropy,* and ozone is spoken of as an allotropic modification of oxygen.

Preparation of Ozone. — Every one has noticed the peculiar odor about an electrical machine which has been in operation for a time. The same odor was observed by the Dutchman, Van Marum, as early as 1785, when an electric spark was passed through oxygen. This gave the key to the preparation of the substance, which was discovered in 1840 by Schönbein. When an electric spark is passed through oxygen the volume of the gas diminishes and the result is a mixture of oxygen and ozone.

Ozone is formed in larger or smaller quantities under a number of conditions. When phosphorus is exposed to the air it undergoes slow oxidation, and at the same time some of the oxygen of the air is converted into ozone.

Ozone is also formed in small quantities in certain reactions where

oxygen is liberated. The oxygen set free when sulphuric acid acts on manganese dioxide contains a detectable amount of ozone.

When water acidulated with sulphuric acid is electrolyzed, the oxygen liberated at the anode contains an appreciable amount of ozone.

When barium dioxide is treated with sulphuric acid, the oxygen set free contains a very considerable amount of ozone.

The best method, however, of obtaining ozone in quantity is by passing electricity through oxygen.

A convenient form of apparatus for preparing ozone is the following (Fig. 5): Into the glass tube *GG* an iron tube *II* is inserted. The glass tube is surrounded for a part of its length by tin-foil. Oxygen

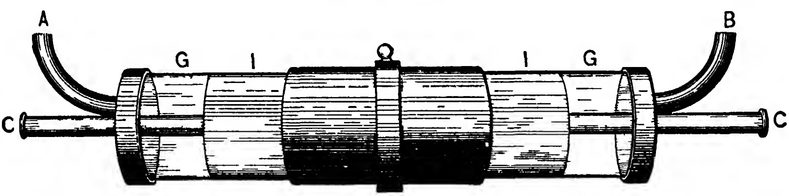


Fig. 5.

is introduced into the glass tube through the tube *A* and escapes through *B*. A current of water is passed through the tube *CC* to keep the apparatus cool. The tin-foil, on the one hand, and the tube *C*, on the other, are connected with the poles of an induction machine. Silent discharges take place between the tin-foil and the iron, passing through the oxygen. Under these conditions a part of the oxygen is converted into ozone.

Properties of Ozone. — The property by which ozone is most easily recognized is its irritating odor, whence the name. Ozone, like oxygen, is a gas under ordinary conditions, but can be converted into a dark blue liquid. It can be detected most easily chemically by its action upon a colorless solution of potassium iodide. A dark brown color appears in such a solution when ozone is passed through it. This we shall learn is due to the oxidizing action of the ozone, liberating iodine. This method of detecting ozone was regarded for a long time as furnishing evidence that it exists in the atmosphere. It has, however, been found that there are other substances which color a solution of potassium iodide as well as ozone, and we are still in doubt as to whether ozone exists in the atmosphere. If it is present at all in the atmosphere, it is quite certain that it exists only in very small quantities.

Ozone is, in general, a much more active substance chemically than oxygen. It has, therefore, come to be known as "active" oxygen. It has much greater oxidizing power than oxygen, especially at ordinary temperatures. It will effect oxidations which, at the same temperature, oxygen is entirely incapable of producing. Thus, ozone will oxidize a piece of metallic silver at ordinary temperatures, covering it with a layer of brown oxide, while under similar conditions oxygen is not able to effect such an oxidation.

Transformation of Ozone into Oxygen. — We have seen that oxygen is transformed into ozone under the influence of the silent electrical discharge. The question naturally arises, Can ozone once formed be transformed again into oxygen? The answer is it can. When ozone is heated to 300°, it passes back into ordinary oxygen. We can thus pass either from oxygen to ozone or from ozone to oxygen.

This raises the important question, What is the cause of the difference in properties between the two modifications of oxygen as it is usually stated? Since either modification can be transformed into the other, it is obvious that there is some close connection between them.

The Difference between Oxygen and Ozone. — It is obvious from what has been stated that there is a marked difference between the properties of oxygen and ozone, yet ozone materially considered is oxygen and nothing but oxygen. How can we account for the difference in the properties of these two substances?

In dealing with the external universe we must not confine our attention to what we are pleased to call matter, which is pure theory and cannot be perceived as such by our senses, but must take into account especially the various manifestations of energy; since all that we can learn through our senses are changes in energy or energy differences. In thinking of element or compound we are liable to lay too much stress upon the material side, because we fancy that it is this side which appeals to our senses, and to overlook or deal lightly with the chemical or intrinsic energy which is stored up in the substance. Every chemical compound has a greater or less amount of intrinsic energy stored up within it, and its chemical properties are largely conditioned by this intrinsic energy. With this conception clearly in mind we may approach the problem of the difference between oxygen and ozone.

The Same Kind of Matter but Different Amounts of Energy. — We have already seen that oxygen and ozone are made up of the same kind of matter, since each is transformable into the other. If we

study this side of the problem quantitatively, we shall find that when three volumes of oxygen are converted into ozone, the resulting gas occupies only two volumes. Thus, if three litres of oxygen were converted into ozone, only two litres of ozone would be formed. On the other hand, if two litres of ozone were decomposed by heat, three litres of oxygen would be formed.

To anticipate what we shall understand more clearly later, the atom of oxygen cannot exist by itself in the free state, but two atoms of oxygen always unite and form what is called the molecule of oxygen. In oxygen gas, as we ordinarily know it, we do not have the atoms of oxygen uncombined with one another, but the molecules which are formed by the union of two atoms.

It has been shown that in the molecule of ozone there are three atoms of oxygen, while in the molecule of oxygen there are only two. It is obvious, however, that the difference in the number of atoms in the molecule, alone considered, is not sufficient to account for such differences in properties as exist between oxygen and ozone. Indeed, it is difficult to see how this would produce a difference in any property other than the mass of the molecule.

The real difference in the properties of oxygen and ozone is due to the different amounts of intrinsic energy present in their molecules. This statement is not made dogmatically, but can be demonstrated experimentally in the following manner: —

When carbon is burned in oxygen the product is carbon dioxide. When carbon is burned in ozone the product is carbon dioxide. We start in both cases, with the same substance, carbon, and we end with the same product, carbon dioxide. Any differences in the two reactions must be due to the differences between the oxygen and the ozone.

If we measure the *amounts of heat* liberated in the two reactions, we find that they are very different indeed. Considerably more heat is evolved when carbon is burned in ozone than when carbon is burned in oxygen. This shows that there is *more intrinsic energy present in the molecule of ozone than in the molecule of oxygen.*

This result is just what we would expect from the chemical behavior of the two modifications of oxygen. Ozone is the more active chemically, and ozone contains the larger amount of intrinsic energy. This alone serves to show the importance of energy relations in dealing with chemical phenomena.

CHAPTER IV

HYDROGEN (At. Wt. = 1.008)

Occurrence.—Hydrogen, which was discovered by Cavendish in 1766, is apparently the most widely distributed of all the elements. It occurs in the earth's atmosphere in very small quantities. It occurs in the sun, especially in the prominences seen during solar eclipses, in the stars, and even in the nebulous masses scattered throughout the universe. It has been found in certain great salt deposits, as those of Salzburg, Germany, in meteoric iron, and in connection with natural petroleums.

The greatest amount of hydrogen on the earth, by far, is in water, whence the name (*hydor*, water, and *gennao*, to produce). All water contains 11.19 per cent of hydrogen, and when we consider the amount of water upon the earth, we get some idea of the amount of hydrogen present on our globe. It also occurs in most forms of living matter.

Preparation of the Element Hydrogen.—To obtain the element hydrogen, we would naturally turn to water as the largest source. Hydrogen can be obtained from water by several means. When a little acid is added to water and the electric current passed through the acidified water, hydrogen gas is liberated at one of the poles, and can be easily collected.

Hydrogen can also be obtained from water by purely chemical means. When water-vapor is passed over highly heated iron, the iron combines with the oxygen in the water-vapor, and hydrogen is set free. The equation expressing this reaction is—

$$3\ Fe + 4\ H_2O = Fe_3O_4 + 4\ H_2.$$

There are certain elements which combine with the oxygen of water even at ordinary temperatures, liberating the hydrogen. Such an element is metallic sodium. When metallic sodium is brought in contact with water at ordinary temperatures, a violent reaction takes place, in the sense of the following equation:—

$$2\ Na + 2\ H_2O = 2\ NaOH + H_2.$$

When potassium is used instead of sodium, a still more violent reaction takes place: —

$$2\,K + 2\,H_2O = 2\,KOH + H_2.$$

In practice we seldom use any of the above methods, since we have means of preparing hydrogen on a large scale which are far more convenient than any of these. When zinc is treated with a strong acid, such as hydrochloric or sulphuric, the metal passes into solution and the hydrogen from the acid escapes. In the case of hydrochloric acid and zinc, this is represented by the following equation: —

$$Zn + 2\,HCl = ZnCl_2 + H_2.$$

In the case of zinc and sulphuric acid by the following equation: —

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

Hydrogen is readily prepared as follows: Introduce some pieces of zinc into a glass flask, *A*, as shown in the figure (Fig. 6), and pour dilute hydrochloric acid into the flask through the funnel-tube *B*, until the end of the tube dips beneath the acid. Hydrogen gas will be liberated and escape through the side tube *C*.

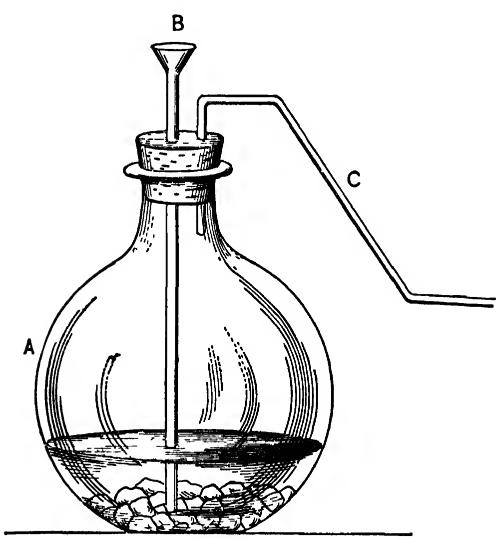


Fig. 6.

The gas can then be passed through a wash-bottle filled with water to remove any trace of acid, and afterwards dried by passing through tubes containing calcium chloride, sulphuric acid, or phosphorus pentoxide.

If it is desired to prepare hydrogen on a still larger scale, a form of apparatus devised by Kipp is very convenient. From this apparatus hydrogen is obtained by simply turning a stop-cock. When no more gas is desired the stop-cock is closed, and the pressure of the hydrogen generated, automatically drives the acid away from the zinc and causes the further liberation of gas to cease.

Combination of Hydrogen with Oxygen.—Hydrogen, a colorless and odorless gas, combines readily with oxygen at elevated temperatures. A mixture of hydrogen and oxygen can be kept for an indefinite time, provided the mixture is not heated. If the temperature is raised sufficiently, the two combine with the greatest ease, producing a violent explosion.

That hydrogen can be burned in the presence of oxygen without any explosion taking place can be shown by the following experiment: Attach a rubber tube to the end of the small glass tube *C* (Fig. 6), and insert into the other end of the rubber tube a metallic tube with a very fine opening. The small tube at the end of a mouth-blowpipe works very well. Allow the hydrogen to escape from the apparatus through the metallic tube until every trace of air has been removed from the apparatus. Then ignite the hydrogen at the end of the metal tube. It will burn with a flame which is nearly colorless, but which is intensely hot, as can be shown by inserting a piece of metal into the flame.

The reaction which takes place between the hydrogen and the oxygen of the air is represented by the following equation:—

$$2\,H_2 + O_2 = 2\,H_2O;$$

the product formed is ordinary water.

That water is formed in this process can be readily demonstrated as follows: Bring a cold, dry, glass cylinder over the flame of burning hydrogen, and hold it in position for a few moments. The inner wall of the cylinder will quickly become covered with moisture, and after a short time drops of water will form on the walls of the cylinder and drop from the mouth.

The explosive nature of the mixture of hydrogen and oxygen can be readily demonstrated by the following experiment: Mix two volumes of hydrogen gas with one volume of oxygen gas, and conduct some of the mixture through a solution of soap until a mass of soap bubbles has been formed. The solution of soap should be placed in a thick-walled, porcelain, evaporating dish. Place the dish containing the soap bubbles in a protected place, such as under the hood, and bring the flame of a gas-lighter carefully up to the bubbles filled with the mixture of hydrogen and oxygen. An explosion will take place whose violence depends on the size and number of bubbles present. It is well, therefore, not to have any great amount of the mixed gases present when the flame is applied.

This mixture of the two gases containing two volumes of hydrogen to one of oxygen is known as *electrolytic gas* or *detonating gas,*

since it is the same mixture which is obtained when an electric current is passed through acidulated water and the gases liberated at the two poles allowed to mix.

Mixture of Hydrogen and Oxygen affected by the Presence of Certain Substances. — We have seen that hydrogen and oxygen will remain in the presence of each other uncombined for an unlimited time, provided the temperature to which the mixture is subjected is not too high. Such a mixture is very materially affected by the presence of certain substances. If a piece of ordinary platinum foil is introduced into a mixture of hydrogen and oxygen, the volume of the mixed gases rapidly diminishes, showing that combination has taken place, and water is formed. Platinum sponge acts still more effectively than platinum foil, probably on account of the much larger surface which it exposes.

One peculiarity of the above reaction is that the platinum does not undergo any change, itself not entering into the reaction; and further, that a very small amount of platinum may cause an enormous quantity of hydrogen and oxygen to combine.

Other metals produce the same effect, although to a less extent than platinum, and often require a higher temperature to cause any appreciable amount of combination between the two gases.

A special name has been applied to reactions brought about by the simple contact with some foreign substance. They have been termed *catalytic.*

Catalytic Reactions and Catalyzers. — The above is far from being an isolated example in the field of chemistry. On the contrary, it is a type of a large number of reactions. Such reactions, however, have certain features in common which enable us to classify them. In all catalytic reactions the substance which effects the reaction — the catalyzer — does not enter into the reaction. Secondly, a very small amount of the catalyzer can effect relatively an enormous amount of chemical combination. As the subject develops we shall encounter a number of catalytic reactions, and the whole subject of catalysis and catalyzers has come very much to the front in the last few years. The opinion is rapidly growing that catalysis plays a very important part in connection with the life processes, and underlies many of the chemical transformations which are taking place in the living body.

Relations by Volume in which Hydrogen and Oxygen Combine. — It was discovered early in the nineteenth century that hydrogen and oxygen combine in simple volume relations. No matter in what proportions the gases hydrogen and oxygen are mixed, for every

volume of oxygen which disappears when combination takes place two volumes of hydrogen disappear. The ratio of the volumes which combine is, therefore, one to two.

The further question which remains is what relation exists between the volumes of the gases which combine and the volume of the water-vapor formed. The simplest relation would be that the volume of the water-vapor would be equal to the sum of the volumes of the oxygen and hydrogen which have entered into combination. Such a relation, however, does not exist. The volume of the water-vapor formed is less than the sum of the volumes of the gases which have combined. This is the same as to say that when hydrogen and oxygen combine there is a contraction in volume.

The relation which actually exists is, however, comparatively simple. Two volumes of hydrogen gas combine with one volume of oxygen gas and form two volumes of water-vapor. Three volumes of the constituent gases have disappeared, and two volumes of the product have been formed. There has been a contraction in volume of one-third.

We shall learn from a study of other cases that this is a general relation. In the first place, gases combine in simple volume relations, and in the second, there is a simple relation between the volumes of the gases which enter into combination and the volume of the product formed.

Heat Energy produced when Oxygen and Hydrogen Combine. — That there is a large amount of heat energy produced when oxygen combines with hydrogen is shown by the fact that the vessel which contains the gases becomes appreciably heated. The amount of heat which is produced in this reaction has been carefully measured. When 2 grams of hydrogen combine with 15.88 grams of oxygen, the heat set free is 68.360 calories.

This is an unusually large quantity of heat to be produced by such small quantities of substances entering into chemical reaction. It has been utilized as a source of very high temperature in a form of lamp which we shall now describe.

The Oxyhydrogen Blowpipe. — The oxyhydrogen blowpipe is a form of apparatus in which hydrogen is so burned in oxygen as to concentrate the heat in a small space. The apparatus is represented in Fig. 7. The hydrogen enters through the side-tube *H*, and is lit at *E*. Oxygen enters through the tube *O* and does not mix with the hydrogen until the flame is reached. If it mixed with the hydrogen before reaching the flame, we would have electrolytic gas, or detonating gas as it is sometimes called, and it would explode violently when a flame was applied to it.

The flame of the oxyhydrogen blowpipe gives very little light, but is intensely hot. It will give some idea of the temperature of the flame to state that platinum can be easily melted in it.

While the flame of the oxyhydrogen blowpipe is itself only slightly luminous, an intense light can be produced by allowing it to fall upon certain substances which can be heated to a high temperature without fusion. Such a substance is ordinary lime. When the oxyhydrogen flame is allowed to fall upon a cylinder of

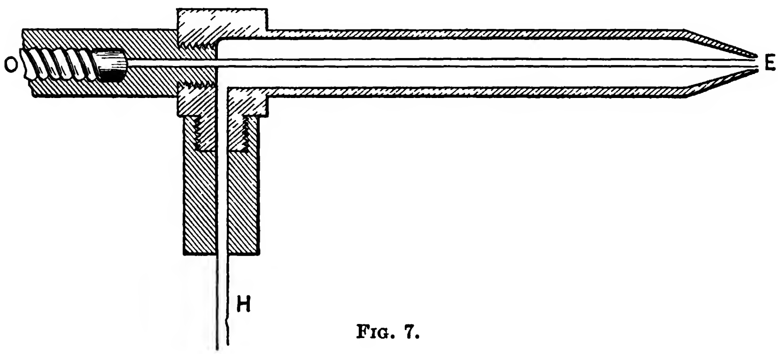


FIG. 7.

lime, an intense white light is produced. This is the *Drummond light.* The light is so intense that it can be used where high illumination is required, as in projecting lanterns and the like.

Dry Hydrogen will not combine with Dry Oxygen. — It would be gathered from what has been said thus far that hydrogen and oxygen always combine if the temperature to which they are subjected is sufficiently high. This is not the case. If very great precautions are taken to remove every trace of moisture from both the oxygen and the hydrogen, the mixture of the two gases may be heated above 700° — far above their ignition temperature — without the slightest combination taking place. The significance of this fact cannot be seen at present, but will become obvious as the subject develops. It lies at the foundation of what we believe to be the true explanation of the cause of chemical action.

The Reducing Power of Hydrogen — The tendency of hydrogen to combine with oxygen manifests itself, not only when the oxygen is in the free state, but even when it is combined with other elements. Hydrogen has the power of removing oxygen from its compounds with other elements, especially at somewhat elevated temperatures. The removal of oxygen from a compound is known as *reduction*, and the substance which can remove the oxygen as a *reducing agent.*

Take the oxide of zinc, which has the composition ZnO. When hydrogen is passed over this substance at an elevated temperature, it combines with the oxygen and leaves the zinc reduced to the elementary condition.

$$ZnO + H_2 = H_2O + Zn.$$

Similarly, when oxide of iron is heated in the presence of hydrogen gas, the oxygen combines with the hydrogen, forming water, and leaves the iron in the free condition.

$$Fe_3O_4 + 4\ H_2 = 4\ H_2O + 3\ Fe.$$

This reaction may occasion some surprise when it is recalled that one of the methods described for making hydrogen was to pass water-vapor over highly heated iron. The iron combined with the oxygen of the water and set hydrogen free. Now we have exactly the reverse taking place, hydrogen combining with the oxygen of iron oxide setting iron free. Reactions of this kind, which can proceed either way, — either from left to right, as we write our chemical equations, or from right to left, — are known as *reversible*. The way in which the reaction will proceed is conditioned solely by the relative quantities of the substances present. If there is a large amount of water-vapor present, the reaction will proceed thus: —

$$3\ Fe + 4\ H_2O = Fe_3O_4 + 4\ H_2.$$

If, on the contrary, there is a large amount of hydrogen present, thus: —

$$Fe_3O_4 + 4\ H_2 = 3\ Fe + 4\ H_2O.$$

This it the first time that we have encountered the *effect of quantity or mass* on chemical activity.

We shall learn that reversible reactions are the rule and not the exception in chemistry, and that the effect of mass or mass action has been formulated algebraically, and is one of the fundamental generalizations upon which the science of chemistry rests.

Compounds of Hydrogen with Other Metals. — Hydrogen forms compounds with a number of other elements, and some of these are among the most important compounds known to the chemist. Thus, hydrogen combines readily with sulphur and analogous elements, forming with sulphur the compound H_2S, with selenium H_2Se, and with tellurium H_2Te. It combines with chlorine and allied elements, forming one of the most important classes of acids; the best known member of which is hydrochloric acid. It combines with nitrogen,

forming the well-known base ammonia (NH_3). Hydrogen also combines directly with a number of the metals and forms definite compounds with these substances. These are known as *hydrides.* The compound with palladium is especially well known, having the composition Pd_2H. Hydrogen also combines with sodium and potassium, forming NaH and KH, and with calcium, strontium, and barium, forming CaH_2, SrH_2, and BaH_2. These compounds will, however, be discussed in detail under the several elements in question.

Hydrogen present in All Acids. — We shall learn that the element hydrogen is present in every member of that enormously large class of compounds known as acids. And, further, that it is the hydrogen which gives to these compounds their acid properties. This fact has come to be recognized recently in its full significance through the investigations of physical chemistry. It was thought for a long time that oxygen is the element fundamental to acidity. Indeed, the name means acid former. Compounds were, however, discovered which are the very strongest acids and which contain no oxygen whatever. The attempt which was made to fit these cases in with the oxygen theory of acids will be considered when hydrochloric acid is taken up.

This rôle of hydrogen, where it gives acidity to all compounds possessing it, is by far the most important which it plays in the whole field of chemistry.

Nascent Hydrogen. — When hydrogen is first liberated by the action of a metal on an acid, it has very different properties from those which it possesses after it has once been formed. While hydrogen gas as we ordinarily know it must be heated to an elevated temperature before it will reduce the oxides of most metals, hydrogen which is just being formed will reduce many such substances even at ordinary temperatures. Many other reactions which hydrogen gas will either not effect at all, or effect only at elevated temperatures, will be produced readily at ordinary temperatures by hydrogen which is just being formed.

Hydrogen which is just being formed has acquired a specific name to distinguish it from hydrogen which has been formed for an appreciable time. It is known as *nascent hydrogen.* This condition of the nascent state we shall learn is not peculiar to hydrogen, but is possessed by other elements as well.

The explanation which has been offered to account for the properties of substances in the nascent state is based upon the atomic theory. The hydrogen molecule, like the molecule of oxygen, has been shown by methods which we shall study later, to consist of

two atoms. When hydrogen is first set free, it is very probable that it is in what we at present must call the atomic condition — one atom by itself. This is supposed to be the condition in the nascent state. After the hydrogen atoms have time to come in contact with one another, the atoms combine in groups of two, and we have molecular hydrogen as we ordinarily know it.

PHYSICAL PROPERTIES OF HYDROGEN

Certain Physical Properties of the Element Hydrogen. — Hydrogen is a transparent, colorless, gas, without taste or odor. It is the lightest of all known substances, being nearly sixteen times lighter than oxygen. One litre of hydrogen at normal temperature and pressure weighs only 0.08995 gram. The relative lightness or small density of hydrogen can be shown in a number of ways.

If a small balloon or light sack of any kind which will hold a gas is filled with hydrogen, the mouth tied, and the balloon set free, it will rise rapidly in the air, showing that hydrogen is considerably lighter than air. This is made use of on a large scale by aeronauts for ascending to considerable heights in the atmosphere. A large silk balloon is filled with hydrogen, and it will not only rise in the atmosphere but will carry considerable weight with it. When it is desired to descend, the hydrogen is allowed to escape through a valve into the air.

Another method of demonstrating the small density of hydrogen is the following: Fill a cylinder with hydrogen by displacement of water and cover the cylinder with a glass plate. Place a second cylinder filled with air just over the first and remove the plate of glass. The hydrogen will rise from the lower into the upper cylinder and displace the heavier air, which will fall into the lower cylinder in which the hydrogen was originally present. This can be proved by touching a match to the mouths of the two cylinders after they have been separated. A small explosion in the upper cylinder will show that it contains the hydrogen, while the absence of any appreciable hydrogen in the lower cylinder is shown by the fact that it will not take fire and burn.

A still more striking illustration of the small density of hydrogen is shown by an experiment based upon the *rate at which hydrogen gas diffuses.* There is a well-known law connecting the rates at which gases diffuse with their densities.

Gases diffuse with velocities which are inversely proportional to the square roots of their densities.

The lighter the gas, the more rapidly, then, will it diffuse. That hydrogen diffuses rapidly can be shown by the following experiment (Fig. 8): A hollow, porous cup *C* is fastened to a glass tube *R*, which extends into the flask *F*, passing through a stopper which tightly closes the mouth of the flask. A second glass tube *T*, drawn out to a fine opening, passes through a second hole in the stopper and dips beneath the water in the flask. A large glass vessel *V* is now

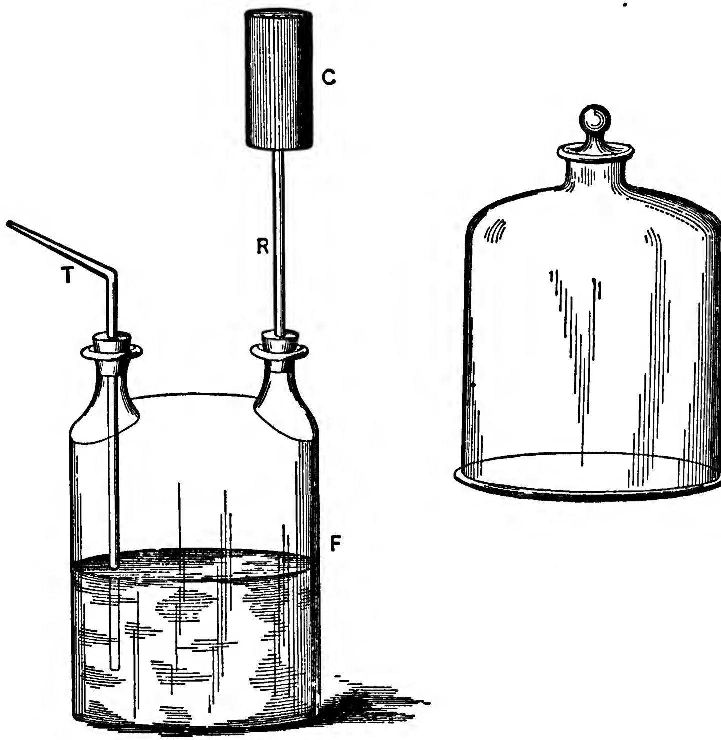


Fig. 8.

filled with hydrogen and placed over the porous porcelain cup. Hydrogen diffuses rapidly in through the cup, due to the small density of the gas, produces a pressure inside the apparatus, and this forces the water up into the glass tube *T*, and out through the small opening. In this way quite a fountain can be produced.

Hydrogen is only slightly soluble in water, 100 volumes of water at 15° dissolving only 1.9 volumes of hydrogen.

The Liquefaction of Hydrogen. — Hydrogen like oxygen was one of the few gases which resisted liquefaction until quite recently.

It was, therefore, placed by Faraday and the earlier investigators among the "permanent gases." Like oxygen it was subjected to enormous pressures by Natterer and others, but they were not able to liquefy it because it was not cooled to its critical temperature. The critical temperature of hydrogen is very low indeed, $-242°$, and at first sight it is not easy to see how such a temperature can be reached. When liquid oxygen is allowed to evaporate under small pressure, a temperature of $-210°$ to $-220°$ can be secured, but this is still above the critical temperature of hydrogen. If, however, hydrogen under a pressure of several hundred atmospheres is cooled to $-200°$ or $-220°$ and then is suddenly allowed to expand, it will in expanding cool itself to its point of liquefaction. The critical pressure of hydrogen is less than 20 atmospheres.

The liquefaction of hydrogen in appreciable quantities we owe almost entirely to Dewar. He has established its boiling-point to be $-252°$. It is, however, possible to reach a still lower temperature by a method which has now become familiar to us. By allowing liquid hydrogen to boil under greatly diminished pressure, still further cooling is produced, and a temperature as low as $-258°$ has been realized. Under these conditions the hydrogen solidified. The freezing-point or the melting-point of hydrogen has been shown by Dewar tc be $-258°$. It should be observed that this is only 15° above the absolute zero.

We naturally ask the question, How can such *low temperatures be measured?* All ordinary forms of thermometers are, of course, useless long before any such temperatures are reached, alcohol solidifying easily in liquid oxygen. Even the air thermometer, based upon the change in volume of air with change in temperature, fails at such low temperatures, because the laws of gas-pressure do not hold near the point of liquefaction of a gas, and air is easily liquefied by contact with liquid hydrogen.

The best form of thermometer for measuring such low temperatures is what is known as the platinum thermometer. This is based upon the fact that the resistance to the passage of an electric current offered by a metal wire changes with change in temperature. The lower the temperature the less the resistance offered to the passage of the current. A platinum wire is used for several reasons, one of them being that platinum is not acted upon by many substances.

Even the platinum thermometer at such low temperatures is not capable of measuring the temperature very accurately, since relations which obtain at higher temperatures probably do not hold accurately in the regions of such extreme cold. It is, however, probable, all

things considered, that temperatures such as those of liquid hydrogen can be measured to within a few degrees.

Can the Absolute Zero be realized Experimentally. — The further question arises, Is there any possibility of reaching the supposed absolute zero? We are compelled to answer that as far as we can see at present there is no such possibility. There is only one substance known (helium) which boils lower than hydrogen, and this, probably, only slightly lower. Further, the amount of helium which can be obtained is apparently so small that we can scarcely hope to use it for obtaining much lower temperatures than those already realized.

If helium existed in sufficient quantities, we could liquefy it, allow the liquid to boil under diminished pressure, and in this way secure a temperature several degrees below the boiling-point of this element. From what is known at present of the probable boiling-point of helium, it is safe to say that even under these conditions a temperature as low as $-273°$ could not be realized. In order that this temperature should be reached, some substance must be discovered whose boiling-point is considerably below that of hydrogen. Until such is obtained it is idle to predict the realization experimentally of the supposed absolute zero of temperature, $-273°$.

Properties of Liquid Hydrogen. — Liquid hydrogen is colorless and transparent and has small viscosity. The supposed blue color of liquid hydrogen is due to impurities. It has a density of 0.07, water being unity. By contact with liquid hydrogen, oxygen (and as we shall learn also air) is converted first into a liquid and then into a solid, or is frozen, as we say.

A beautiful and thrilling experiment has been performed by Dewar, who has liquefied hydrogen by the litre. Liquid hydrogen was poured into a test-tube and the tube exposed to the air. Liquid air soon began to stream off the test-tube, and finally the tube became covered with frozen air. The remarkable character of this experiment is evident to any one.

The Hydrogen Spectrum. — The spectrum lines of hydrogen are very characteristic. A capillary glass tube is enlarged at both ends and completely exhausted. It is then filled with hydrogen gas at a low pressure, and sealed off. An electric discharge is passed through the tube between the two platinum terminals fused into the two ends of the tube. The light emitted when the discharge is passed through the hydrogen is purplish red. When this light is analyzed by means of the spectroscope, two very bright lines and one faint line are observed.

The *spectroscope* consists of a prism through which the light is passed. Light of different wave-lengths is refracted differently, and we have a separation of the several wave-lengths from one another. When white light is viewed through a spectroscope, it is broken up into the spectrum colors. When the light emitted by a gas is passed through a spectroscope, bright lines appear, and not a continuous spectrum. The light emitted by hydrogen when analyzed spectroscopically shows a bright green and a bright red line, and a faint line in the violet. Lines in exactly these positions are shown by no other substance. When sunlight is analyzed spectroscopically, we find dark lines in exactly the positions occupied by these bright lines of hydrogen. These are also due to hydrogen, and illustrate the general principle that a gas *absorbs exactly the same wave-lengths which it can itself emit.* This is the law of Bunsen and Kirchhoff. White light from the interior of the sun, passing through hydrogen in the exterior, has those wave-lengths absorbed which the hydrogen itself can emit. By means of the spectroscope, and by this alone, are we able to prove the presence of hydrogen and other terrestrial elements in the sun.

Another form of spectroscope should be referred to. When white light is thrown upon a metallic surface containing a great number of parallel lines, it is dispersed to even a much greater extent than when passed through a prism. The concave-grating spectroscope of Rowland has proved of incalculable service in spectrum analysis.

Electrolysis of Hydrogen.—J. J. Thomson, by means of electrolysis, separated hydrogen into a positively and a negatively charged constituent. A glass tube across whose centre was placed a loosely fitting aluminium septum was filled with hydrogen. This was subjected to an electrical discharge from the two platinum electrodes fused into the two ends of the tube. After a time the spectrum of the hydrogen on the two sides of the septum was observed. On the one side the green hydrogen line was very prominent and the red faint, while on the other side the red line was very prominent and the green light faint.

The hydrogen gas was thus electrolyzed into a positive and a negative constituent, the one being characterized by the strong green line, and the other by the bright red line. The hydrogen molecule, like the molecules of chemical compounds, is, therefore, made up of a positive and a negative constituent.

CHAPTER V

WATER AND HYDROGEN DIOXIDE

Occurrence of Water. — Water is probably the best known chemical compound, on account of its very wide distribution over the surface of the earth. In the free condition it covers about three-fourths of the surface of the earth. Further, it is widely distributed through the rocks over the surface of the earth, each cubic metre of rock containing on the average about one litre of water. It exists in large quantities in the atmosphere, in the form of water-vapor. It also exists in combination with a large number of substances as *water of crystallization,* or *water of hydration.* Its presence is not limited to inorganic or inanimate nature. *It forms an essential part of all living matter.* If living matter, animal or vegetable, is heated above one hundred degrees, there is an enormous loss in weight, and this is mainly due to loss in water which is driven off. The main constituent of living matter as far as mass is concerned is water. The human body is more than two-thirds water, and the animal and vegetable food which we eat contains scarcely less water in proportion to solid matter. We can thus see why animals can live without food much longer than without water, and why water is absolutely essential to vegetable and animal life.

Water as it occurs in Nature is Impure. — It is safe to say that all natural water contains impurities. This does not refer to impurities which are thrown into water artificially, as by the drainage of human habitations, but to impurities which we may call natural. The water of the sea is very impure because of matter dissolved from the soil and rocks by the waters before they reach the sea, and after they have been poured into it. The waters of small streams and rivers are impure for the same reason. They dissolve a part of the solid matter over which they run and with which they may otherwise come in contact, and carry it along in solution as they make their way down to larger bodies and ultimately to the sea. It is, then, obvious that any water which has come in contact with the earth would be impure. There are, however, very different

degrees of purity represented by terrestrial waters. If the water has come in contact with certain substances, it will be very much more impure than by contact with other substances. If water has come in contact with soil containing a large amount of limestone, and especially if there is much organic matter in the soil, it will dissolve large quantities of the limestone and is then what we call *hard water.*

If, on the other hand, the water has fallen upon a region which contains mainly sandstone or other difficultly soluble rocks, but little of the solid matter will dissolve, and we have then comparatively pure water. This is the reason why water from mountains composed of sandstone is relatively pure. Further, water from mountains comes in contact with relatively little soil, and rocks in general are much less soluble than soils.

While it is obvious that water which has once fallen upon the earth must be more or less impure, the question might reasonably be asked, Is not rain-water which has never come in contact with the soil fairly pure? This question is the more reasonable since it is known that when water is evaporated, as by the heat of the sun, from the sea and land, most of the impurities remain behind.

Rain-water would undoubtedly be fairly pure were it not contaminated while in the atmosphere. However, while it exists in the atmosphere in the form of vapor it takes up many kinds of impurities, and especially after it is formed into drops and falls through the atmosphere, some foreign matter is dissolved by it. Indeed, according to a well-established theory raindrops form around dust particles in the atmosphere and carry these particles down with them as they fall. This is undoubtedly the reason why the atmosphere seems so pure after a heavy rainstorm.

From the above it is then obvious that all natural waters contain impurities, but that the amount of impurity varies greatly from one sample of water to another.

Mineral Waters. — In certain localities minerals exist which are more or less soluble in water. Rain-water or water from other sources dissolves these substances and holds them in solution. Such waters are known in general as *mineral waters,* the nature of the water depending upon the nature of the mineral in solution. At the great sources of mineral waters, such as Saratoga, New York, there are beds of various salts deposited beneath the surface of the earth, some of them nearer the surface, others at much greater depths. When the waters percolate through such regions, they come in contact with these various deposits, and dissolve more or

less of the different substances, the amounts dissolved depending upon the relative solubilities.

These substances give characteristic tastes and other properties to the water in which they are present, and thus we have the various mineral waters which are so well known and so much sought after.

If the water percolates through a soil containing large amounts of carbon dioxide set free from decomposing vegetable matter or from other sources, and especially if it comes in contact with carbon dioxide under high pressure, large amounts of the gas may dissolve in the water and be carried by it to the surface of the earth or to a mineral well which has been bored below the surface. Such waters are known as *effervescent,* since they give off a part of the dissolved carbon dioxide when exposed to the air. In other cases the water dissolves considerable hydrogen sulphide and gives us what is known as *sulphur water.* When other substances are dissolved in the water, they give their characteristic properties to it, and thus we have the almost endless variety of mineral waters which are present upon the market with their ludicrously pedantic names.

Purification of Water. — Water is usually rendered impure in the way described above, by carrying with it in solution dissolved substances. It may, however, be rendered impure by matter which is not in solution, but simply in a state of mechanical suspension. This latter condition is illustrated by small streams after a heavy rain. The finely divided soil is carried along with the water in a state of fine suspension, and we have *muddy water.*

When the impurity is in a state of mechanical suspension and is not in solution, it can be removed by *filtration.* Filtration consists in passing water through a substance with very fine openings or pores, so fine, indeed, that the particles of water can pass, but not the particles held in mechanical suspension. This is effected on a small scale in the laboratory by means of certain varieties of paper known as "filter paper." If it is desired to purify on a large scale water which contains foreign matter in suspension, some other device must be resorted to. It is sometimes passed through a thick layer of very fine sand, and other substances have been used.

Filtration is of fundamental importance to the chemist, especially in connection with analytical operations. Quantitative analysis depends largely upon the precipitation of the substance whose quantity we wish to determine in the form of a solid. This solid must then be filtered off from the liquid which is present and carefully washed before it can be dried or ignited and weighed.

If the impurity in the water is in solution, it is obvious that we

cannot separate it by any mechanical process such as filtration. Some other principle must be utilized. When water containing non-volatile impurities is boiled, the vapor which escapes is practically pure. If this vapor is condensed again, we have practically pure water. This process of converting a liquid into vapor and recondensing the vapor is known as *distillation,* and the apparatus in which a distillation is carried on as a *still.*

Distillation, like filtration, is of fundamental importance in the chemical laboratory. The water which is furnished a chemical laboratory from natural sources is not sufficiently pure to be employed in any chemical operation. Before it can be used it must be distilled, and in all chemical work only distilled water is employed.

The form of still which is used when only a small amount of liquid is to be distilled is shown in Fig. 9. Into the glass flask

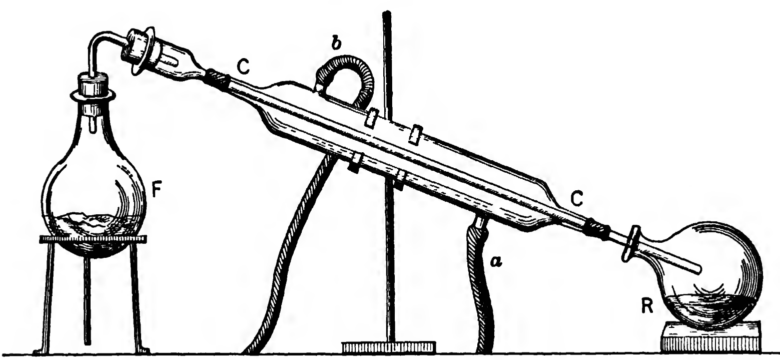


FIG. 9.

F. the liquid to be distilled is introduced. This is heated and converted into vapor by a burner placed beneath the flask. *C* is the condenser, consisting of a small inner glass tube surrounded by a much larger glass jacket. Cold water is passed into the jacket at *a*, and out at *b*. The vapor in the inner tube is condensed to a liquid as it passes through the condenser, and flows into a receiver, *R*.

If it is desired to distil a liquid on a large scale, the form of the apparatus is greatly modified, but the principle is exactly the same as in the apparatus described above.

Another method of purifying water is by freezing it. Just as the vapor which separates from impure water is pure, just so the ice which freezes out of impure water is practically pure. When impure water is partly frozen in a quiet place, the ice which separates con-

tains much less impurity than the water from which it separated, the impurity remaining for the most part in the unfrozen water.

This method of *freezing*, or *crystallization*, is far less efficient and much slower to carry out than the method of distillation, but has value in the laboratory in certain connections.

Water not an Element, but a Compound. — Water is the first substance which we have thus far studied which is not an element, but is composed of more than one element. For a long time in the early days of chemistry water was regarded as an element, and together with air, earth, and fire constituted the four chemical elements.

That water is not an element is obvious from our studies of oxygen and hydrogen. We have seen that by electrolysis both oxygen and hydrogen can be obtained from water; and an element, by definition, is a substance which cannot be decomposed into any other substances.

Composition of Water. — We have seen that oxygen and hydrogen can be obtained from water, but this does not show that water contains only these two elements. To answer this question two general methods are available. First, decompose water, and see whether anything but hydrogen and oxygen is obtained. Second, cause oxygen and hydrogen to combine, and see whether water is formed.

The most convenient means of decomposing water is the electric current. When a little acid is added to water to diminish its resistance to the flow of the current, and an electric current is passed through it, it is decomposed. This process of effecting decompositions by means of the current is known as *electrolysis*. The metallic terminals, or poles, have specific names with which it is important to be familiar. The pole which the current leaves and enters the solution is known as the *anode* ; the pole which receives the current from the solution, as the *cathode*.

The only products obtained by the electrolysis of water are the two gases, oxygen and hydrogen, oxygen being set free at the anode and hydrogen at the cathode. That these are oxygen and hydrogen, respectively, can be shown by the fact that the former will ignite a match which has just been extinguished, and the latter will burn with the characteristic hydrogen flame.

If we wish to know the relative volumes of the two gases set free from water, we must collect and measure them.

A convenient form of apparatus for effecting the electrolysis of water and collecting the gases set free is the following: —

Into the two arms *A* and *B* (Fig. 10) of the U-tube are inserted two platinum electrodes. These tubes are completely filled with acidu-

lated water by filling the reservoir *R* to the desired height, and opening the two stop-cocks at the ends of *A* and *B*. The current is passed into the solution through the electrode in *B* and out through the electrode in *A*. The stop-cocks are closed before the current is passed, and oxygen collects in *B*, and hydrogen in *A*. When the current has been flowing for a short time it will be observed that the gas is collecting in *A* faster than in *B*. The tubes *A* and *B* are graduated so that at any moment the amounts of gases set free can be read off at once. After an appreciable amount of gas has collected in *B*, interrupt the current and read the volumes of the gases in the two tubes. It will be found that there is just *twice* the volume of gas in *A* that there is in *B*. Close the circuit, and allow the electric current to flow until a considerably larger volume of the two gases has been set free. Interrupt the current again and measure the volumes of the two gases. It will be found that the volume of the hydrogen is again *exactly double* that of the oxygen.

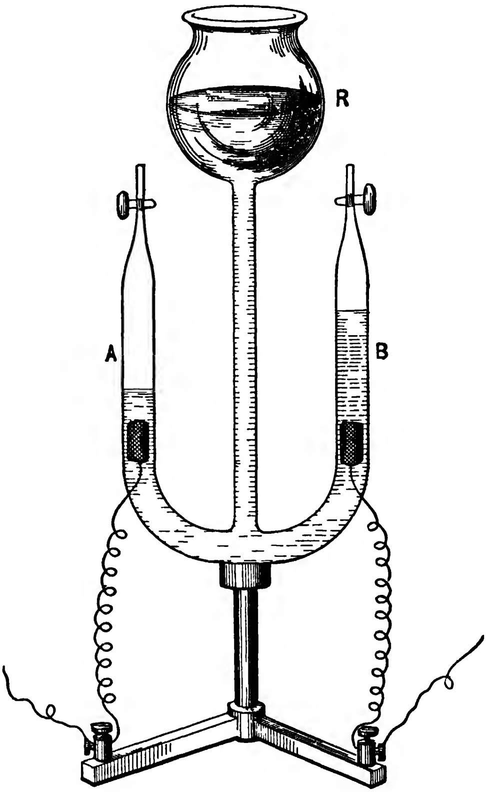


FIG. 10.

No matter how long the current is allowed to flow, nor how much water is decomposed, we would always find that the volume of the hydrogen set free was exactly double that of the oxygen. From the decomposition of water, or by the *analytical method*, we are therefore led to the conclusion that water is made up by the union of two volumes of hydrogen with one volume of oxygen. Since one volume of oxygen weighs 15.88 times one volume of hydrogen, the proportions of hydrogen and oxygen by weight in water are 1 : 7.94. To

determine the composition of water, however, we are not dependent solely upon the analytical method. We can use also the *synthetical.*

If water is composed of two volumes of hydrogen to one volume of oxygen, then, when we mix two volumes of hydrogen with one volume of oxygen and pass an electric spark through the mixture, which causes the gases to combine, all the hydrogen should combine with all the oxygen and form water. This is exactly what takes place. Whenever two volumes of hydrogen are mixed with one volume of oxygen and the gases made to combine by means of an electric spark, or by rise in temperature, all the hydrogen and all the oxygen are used up and water is formed. If more than two volumes of hydrogen are used, all the oxygen will be used up and the excess of hydrogen will remain uncombined. If less than two volumes of hydrogen are used, all the hydrogen will be used up and the excess of oxygen will remain.

The results of synthesis confirm those of analysis; viz. that water is formed by the union of two volumes of hydrogen with one volume of oxygen.

Chemical Behavior of Water. — All things considered, water is probably the most important chemical compound known. It is formed, as we have seen, by the union of hydrogen and oxygen. It is also frequently formed, as we shall learn, by the union of hydrogen with the group OH, this group representing already a combination between oxygen and hydrogen. The possibility of the union of hydrogen in one compound with the group OH, known as hydroxyl, in another compound, conditions a large number of chemical reactions. Indeed, were it not for this fact, the science of chemistry would be very different from what it is to-day.

This naturally raises the question, whence this tendency of hydrogen to unite with hydroxyl? The answer is to be found in the energy relations which obtain in hydrogen and oxygen on the one hand, and in water, on the other. We have seen that when hydrogen combines with oxygen an enormous amount of heat is liberated. This heat is approximately a measure of the difference between the energy in hydrogen and oxygen, and in water. This difference is very great, a large amount of intrinsic energy being converted into heat when hydrogen and oxygen combine.

It is a general principle that whenever a chemical reaction which evolves a large amount of heat can take place, it does so. This is the same as to say that there is a strong tendency on the part of intrinsic energy to pass over into heat, and this is, doubtless, the cause of the strong tendency of hydrogen and oxygen to combine

whenever an opportunity presents itself. The importance of this fact for the whole science of chemistry will become apparent as the subject develops.

Water has the power of combining with a certain class of chemical compounds known as the oxides, converting some of them into the important class of compounds known as the bases, and others into the very important class of compounds known as the acids.

Take the well-known substance lime, CaO. When this is treated with water it combines with it, forming calcium hydroxide: —

$$CaO + H_2O = Ca(OH)_2.$$

As an example of water combining with an oxide, forming an acid, take the trioxide of sulphur, SO_3. When this is treated with water, the following reaction takes place: —

$$SO_3 + H_2O = H_2SO_4.$$

The subject of acids and bases will be considered more in detail when the elements which form these substances are studied.

Water a Stable Compound.— Few compounds known are more stable than water. If we try to decompose it into its elements, we will appreciate what this means. It is true, as we have seen, that it can be decomposed into its elements by means of the electric current, but unless an acid is added to it a current of high voltage is required to effect any appreciable amount of decomposition.

If we try to decompose water into its elements by heat, enormous temperatures are required. In order to effect even slight decomposition a temperature of 1000° or higher is necessary, and a considerable amount of decomposition is effected only when temperatures between 2000° and 3000° are employed.

Stress is laid upon these facts for the purpose of illustrating a general principle. *When a chemical compound is formed with great evolution of heat, it is almost always a very stable substance.* Indeed, the degree of stability can usually be measured by the amount of heat set free during the formation of the substance. We have seen that the heat set free is an approximate measure of the difference between the intrinsic energy of the substances before they unite and the products of the reaction. When there is large heat evolution during a reaction it means, other things being equal, that the products contain relatively little intrinsic energy; and since intrinsic energy is the cause of chemical activity, we should expect those substances with a small amount of such energy to have little chemical activity. To say that a substance is relatively inactive

chemically is, in general, the same as to say that the substance is stable, since stability in the last few years has come to mean chemical inactivity.

PHYSICAL PROPERTIES OF WATER

Physical Properties of Water; Boiling-point. — Water at ordinary temperatures and pressures is a colorless liquid. In very thick layers it has a bluish tint. Under a pressure of 760 millimetres of mercury it boils at 100° C.; *i.e.* at this temperature the tension of the aqueous vapor is just sufficient to overcome the pressure of the atmosphere. As the pressure to which the water is subjected increases, its boiling-point rises. Under a pressure of five atmospheres the boiling-point of water is 152°. Under a pressure of ten atmospheres water boils at 180.3°, while under a pressure of twenty atmospheres it does not boil until a temperature of 213° is reached.

These are the conditions which obtain in a steam-engine. The water is under the pressure of its own vapor, which amounts to from five, to ten or twelve, atmospheres, and consequently its boiling-point is very greatly raised. From the data given above, we can form a pretty close approximation as to the temperature of the water in the boiler of a steam-engine.

Just as water must be heated much higher in the boiler of a steam-engine than in the air in order to obtain boiling, just so it boils much lower on a high mountain than in a valley. As we ascend a mountain the pressure of the atmosphere becomes less, and, consequently, the pressure which the tension of the water-vapor must overcome. On the top of Mont Blanc water boils at about 84°.

As we ascend a mountain the pressure of the atmosphere becomes gradually less, according to a well-known law, so that if we knew the exact temperature at which water boiled at the sea-level at any given time, we could use the temperature at which water boiled at any higher altitude to calculate approximately the height which we had reached.

Heat of Vaporization. — Any one who has ever observed water boil must have been impressed by the enormous amount of heat which is required to convert the liquid into vapor. He must have been further impressed by the fact that the temperature of the vapor is practically the same as that of the liquid from which it was formed. The amount of heat required to convert one gram of

water at 100° into vapor at 100° is 540 calories, *i.e.* the same amount of heat which would be required to raise 540 grams of water 1° in temperature. This is known as the *heat of vaporization of water.*

The Freezing of Water. — When water at ordinary pressure is cooled to 0° it freezes, as we say, or passes into ice. As we cool water down toward its freezing-point, it contracts in volume until a temperature of 4° is reached. As the temperature is further lowered from this point, the water begins to expand and continues to do so until the freezing-point is reached.

The importance of this apparently insignificant fact is very great indeed, from the standpoint of the economy of nature. Since water expands from 4° to the freezing-point, ice is lighter than water and floats upon it. The importance of ice floating upon water and not sinking to the bottom is twofold. In the first place, ice floating upon water protects it from the extreme cold of the atmosphere, since ice is relatively a poor conductor of heat, and in the second place, if ice sank to the bottom of our streams as fast as it was formed, this would continually expose a fresh surface of the water to the cold and our streams might be frozen solid, which would mean the extermination of all living things within them.

Again, if water became continually heavier as its freezing temperature was reached, the coldest water would constantly settle to the bottom, and this would tend to make the stream begin to freeze at the bottom and finally become solid ice.

The fact that water contracts to 4° and then begins to expand again, causing the ice to be formed on the surface of the water and to float there, explains why the rivers and lakes in cold climates are frozen only a few feet in depth, and why the forms of life which inhabit them are not exterminated in one cold winter.

Just as the boiling-point of water is raised by increase in pressure, just so the freezing-point is lowered when the pressure is increased. It may not be obvious at first sight why the freezing-point of water is lowered as the pressure is increased. This can be seen from the following considerations. Water expands in volume from 4° to the freezing-point. Anything which will oppose the expansion will hinder the water from freezing, and under such conditions it will require a lower temperature to freeze the water. The effect of pressure on the freezing-point is, however, small. An increase in pressure of a whole atmosphere lowers the freezing-point of water only about 0°.007.

A pretty and interesting experiment is based upon the above-described fact. Ice at 0° can be melted by simply subjecting it

to pressure. This experiment was shown by Tyndall in his popular lectures as follows. A ray of light was passed through a block of ice which was kept at 0°. The ice was then subjected to pressure, and melting began to take place. The drops of water formed in the interior of the block of ice, having different refractivity from the ice, could be readily seen when the light was thrown on a screen.

Ice has been subjected to such high pressures that it could be melted at −18°.

Heat of Fusion of Ice. — We have just learned what an enormous amount of heat energy must be expended to convert water into vapor. We shall now see that a large amount of heat is required to convert ice into water. The amount of heat required to convert one gram of ice at 0° into water at 0° is 80 calories, *i.e.* the amount of heat which would raise one gram of water from 0° to 80°. This is known as the *heat of fusion of ice.*

Heat of Condensation of Steam and of Solidification of Water. — We have spoken of the heat of vaporization of water being such a large quantity. Just as we have to add a large amount of heat energy to water to convert it into vapor, just so when we recondense the vapor to liquid an enormous amount of heat is set free. This is known as the *heat of condensation* of water. We would naturally ask what relation exists between the heat of vaporization and the heat of condensation of a substance? *The two have been found by experiment to be equal.* That they must be equal follows from the law of the conservation of energy. Starting with water we convert it into vapor and then recondense the vapor to water. The initial and final stages are the same, and the amount of energy added to effect one part of the transformation is given up again when the reverse transformation takes place.

We have seen that considerable heat energy must be added to ice to liquefy it. When liquid water passes over into ice a large amount of energy is given up in the form of heat. This is known as the *heat of solidification.* The heat of solidification of water is exactly equal to the heat of fusion of ice, as has been shown experimentally, and as can be shown from the conservation of energy by reasoning exactly analogous to that used above in the case of heat of condensation.

Superheating and Supercooling of Water. — If water is heated as is usually done, without taking any precautions to remove air and other impurities, it begins to boil at 100° if the barometer stands at 760 millimetres of mercury, or slightly above or below this temperature, depending upon whether the barometer is higher or lower than

the normal pressure. If, however, suitable precaution is taken to purify the water, and to remove all air from it by warming it in a vacuum, it may be heated considerably above 100° without boiling. If water which has been very carefully purified is warmed in a new glass flask, which itself has been carefully cleaned and is free from scratches or any irregularities, it may be heated many degrees above its normal boiling-point without boiling. Water in this condition is said to be *superheated*. When boiling once begins it is liable to take place with explosive violence, as we would expect.

In order that water may be superheated to any appreciable extent it is necessary to take the precautions indicated above, since if there are any impurities present or any irregularities in the vessel used, these will serve as points from which the boiling will begin as soon as the temperature of 100° is reached. The vapor forms readily around such impurities, especially if they are gaseous, as air, or on irregularities, and it is impossible to superheat the water to an appreciable extent. Superheated water is an unstable condition of this substance, and readily passes over into the condition stable at this temperature, *i.e.* vapor. Just as water may be heated above its boiling-point without ebullition taking place, just so it may be cooled below its freezing-point without the separation of ice. When pure water is cooled below 0° without any ice separating, it is said to be *supercooled*. It is much easier to supercool than to superheat water. If ordinary distilled water is placed in a smooth glass tube, which is inserted in a mixture of ice and salt (a freezing mixture which may have a temperature as low as − 20°), and gently stirred as it cools, a temperature of − 4° to − 5° may be reached without any ice separating. If to such supercooled water a fragment of ice as small as can be seen is added, more ice will at once begin to separate, and by vigorously stirring the mixture of ice and water, ice will continue to separate until heat enough is liberated to warm the remaining water up to its true freezing-point, all supercooling being thus removed.

The amount of the solid substance necessary to cause more of the solid to form is so small that we cannot conceive of it, as the German physical chemist, Ostwald, has shown. It is worth noting that in order to remove the supercooling of a liquid it is necessary to use some of the *same substance in a solid state*. If any other solid is used the freezing is not liable to begin and the supercooling may remain; supercooled, like superheated water is an unstable condition. Water does not readily remain in these conditions, but passes over under slight provocation into the condition which is stable at the

temperature in question. From supercooled water ice thus readily separates, just as vapor forms with the greatest ease from superheated water.

The Vapor-tension of Water in its Different States of Aggregation. — The tension of water-vapor is, as we would expect, greatest when the water is in the form of liquid, and least when the water is in the solid state. Ice, however, has a vapor-tension at all ordinary temperatures, and water always has an appreciable vapor-tension at all temperatures at which it remains in the liquid state. The vapor-tension of water at different temperatures and in different states of aggregation has been carefully measured, since the results frequently come into play in many scientific investigations. When these results are plotted as ordinates against temperatures as abscissas, curves are obtained which are of great scientific value, as we shall now see.

The Temperature-pressure Diagram of Water. — In the following diagram (Fig. 11) the ordinate represents the pressure of water-vapor and the abscissa temperature. Water exists, as we have seen, as a solid, a liquid, or a gas, depending chiefly upon the temperature, and also upon the pressure. These states of aggregation are known as *phases*, and water is said to exist in three phases. If we draw the temperature-pressure curves representing the conditions of equilibrium between the different phases of water, the curves will have the form seen in Fig. 11.

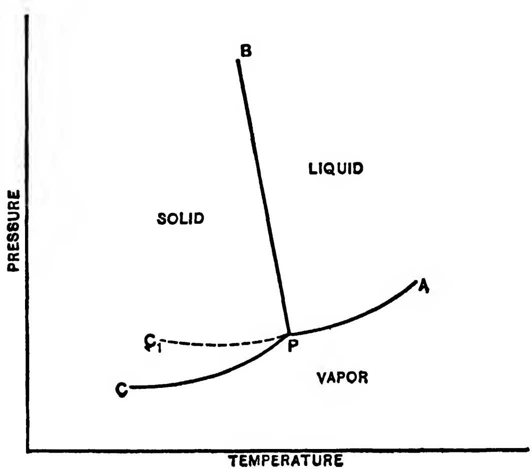


Fig. 11.

The curve *PA* represents the condition of equilibrium between liquid water and water-vapor. Below this curve the vapor is the stable phase, above it the liquid. The curve *PB* is the line of equilibrium between the liquid and the solid phases of water, the liquid being the stable phase to the right of this curve and above the curve *PA*, while the solid is the stable phase to the left of *PB* and above

PC. The curve *PC* is the line of equilibrium between the solid phase of water and water-vapor; above this curve and to the left of *PB* ice is the stable condition, while below this curve and *PA* water-vapor is the stable phase.

It will be observed that the three curves intersect in a point which we have called *P.* This point has properties which make it of special interest. Since it is common to all three curves it means that at this temperature all three phases of water have exactly the same vapor-pressure. That such is the case can be shown by the following considerations. Take the liquid and solid phases. The point *P* represents the temperature at which ice and water are in equilibrium under their own vapor-tension. Since this is much less than an atmosphere, being in fact about four millimetres, the temperature of the point *P* is slightly above zero, since pressure lowers the freezing-point of water. If the vapor-tension of the ice is not the same as that of the water, it must be either greater or less. If it is greater, the ice will vaporize and the vapor condense as liquid; if it is less, the water will vaporize and the vapor freeze to ice. Since, however, by hypothesis this point represents a condition of equilibrium between these phases, where neither can increase at the expense of the other, we could not have either of the above conditions realized. Therefore, since the vapor-pressure of the ice cannot be greater than that of the water at this temperature, and cannot be less, it must be equal to it. A special name has been given to the point *P.* Since it represents a condition of equilibrium between three phases, it is known as a *triple point.* The curves *PA, PB,* and *PC* represent conditions of equilibrium between two phases, and the areas *PAB, PBC,* and *PCA* represent conditions under which only one phase is stable.

The Phase Rule of Willard Gibbs. — We can now state and apply a generalization of wide-reaching significance and of great importance, which holds for conditions of equilibrium such as those with which we are now dealing. This generalization, which was discovered by J. Willard Gibbs, is known as the *Phase Rule.*

We are dealing with one component, water, and three phases, — the solid, liquid, and gaseous. *If the number of phases exceeds the number of components by two, the system is non-variant,* or has no degree of freedom. This means that none of the conditions can be varied without destroying the equilibrium. The triple point *P* is a non-variant system. The number of phases is three and the number of components one, and we cannot vary either the temperature or the pressure without disturbing the equilibrium between the three phases.

If the number of phases exceeds the number of components by one, the system is monovariant, having one degree of freedom. This is the case with the systems *PA*, *PB*, and *PC*. The number of phases is two, and the number of components one, and there exists one variable along these curves. We can vary either the temperature or the pressure, provided we keep on the curve, without destroying the equilibrium between the two phases.

If the number of phases is equal to the number of components, the system is divariant, having two degrees of freedom. This is exemplified by the areas *PAB*, *PBC*, and *PCA*. The number of phases is one, and the number of components one, and two variables exist. We can vary both the temperature and the pressure, provided that we keep within the given area, without in any wise destroying the equilibrium.

The diagram contains in addition to the curves mentioned above the curve PC_1, which calls for special comment. The three curves *PA*, *PB*, and *PC* represent conditions of stable equilibrium. We know, however, that water may be cooled far below its freezing-point without the separation of ice. Water in this state is usually referred to as in unstable equilibrium. Since such conditions simply represent degrees of stability it is better to refer to it as in *metastable equilibrium.*

The curve PC_1 represents a condition of metastable equilibrium for water. The instant a mere fragment of the solid phase is introduced, as we already know, freezing begins and ice separates until the metastable passes over into the stable phase.

Attention must be called to one further point in connection with the temperature-pressure diagram of water. The curves do not run out indefinitely from the point *P*, but stop abruptly in the middle of the diagram. What does this mean ?

Take the curve *PA*, which represents the condition of equilibrium between water and water-vapor. We know that there is a temperature above which the vapor of water cannot be liquefied; the two phases in this region existing as one phase. This is the well-known *critical temperature* of the substance; at the critical temperature we have also the *critical pressure.* These two critical constants for water-vapor are represented by the point *A*, at the extremity of the curve *PA*.

This comparatively simple diagram is, then, a shorthand expression of a large number of experimentally established facts.

Other Physical Properties of Water. — In addition to those physical properties of water already discussed, one or two others will be referred to. Of all known liquids water has probably the highest

specific heat. By the specific heat of water is meant the amount of heat required to raise a given amount of water, say a gram, one degree in temperature. This amount of heat, as we have seen, is one calorie. One calorie of heat will raise a gram of any other known substance more than one degree in temperature. Water thus stands at the head of the list as far as specific heats are concerned.

If we examine the *specific inductive capacity or the dielectric constants* of liquids, we find water either at the very extreme or very nearly the extreme. It seems probable that there is one liquid with a higher dielectric constant, but if so, its dielectric constant is not much higher than that of water.

Similar results would be obtained if we ran through the whole list of properties. Water would stand in practically every case either at the top or bottom of the list of substances. Its properties are, therefore, distinctly extreme. They are either a maximum or a minimum, and usually a maximum.

If we take all the properties of water into account, we shall see that we are easily justified in regarding it as the most remarkable chemical compound known.

Solvent Power of Water. — Water has a remarkable power to dissolve other substances which are brought in contact with it. Indeed, of all known substances it is the best solvent, and with respect to this property it also stands at the very head of the list of chemical substances. The importance of solution for chemistry cannot be overestimated. This becomes obvious when we consider that most chemical reactions take place in solution. Indeed, comparatively few solid substances are capable of reacting with other substances in the solid state. Were it not for solution the whole science of chemistry would be very different from what it is to-day, and far less interesting. Three-fourths, and probably a much larger proportion, of the chemical reactions with which we are now familiar would not take place at all. The reason for this we shall learn a little later.

Water dissolves to a greater or less extent not only most solid substances which are brought in contact with it, but also most liquids and gases.

Unsaturated, Saturated, and Supersaturated Solutions. — When water has dissolved a certain amount of a given substance, but is still capable of taking up more of it, the solution is said to be unsaturated. When water has dissolved all of a given substance which, at the temperature in question, it can take into solution, the solution is said to be saturated. When water contains more of a

given substance than it can hold in a stable condition, the solution is said to be supersaturated.

A saturated solution can be prepared by two methods. First; bring the substance to be dissolved, in excess, in contact with the solvent, and agitate the liquid until it will take up no more of the dissolved substance. This method is slow, and requires a long time for equilibrium to be reached. The second method consists in warming the solvent to a considerably higher temperature, and agitating it at the more elevated temperature with an excess of the substance to be dissolved. It is a general rule to which only a few exceptions are known, that substances are more soluble at higher temperatures than at lower. The solvent at the higher temperature takes up more of the substance than is sufficient to saturate it at the lower temperature. When the solution is cooled down to the temperature desired in the presence of some of the solid substance, the excess of the dissolved substance separates in solid form, and the solution is saturated at the temperature in question.

The results obtained by the second method are always a little higher than those obtained by the first, and it is well to use both methods and take the mean of the results obtained from the two.

To prepare a solution supersaturated at any given temperature we warm the solvent in contact with the substance to be dissolved to a somewhat higher temperature, and allow it to take up all the substance that it can. Every trace of the excess of solid, undissolved substance is then filtered off, and the solution practically saturated at the higher temperature cooled down to the desired temperature. If we are careful to avoid agitating the solution during cooling, we will have a solution supersaturated at the lower temperature.

To determine whether a solution is supersaturated, add a few fragments of the solid phase of the dissolved substance. If there is supersaturation more of the dissolved substance will separate in solid form, until all supersaturation is removed. This explains why it is necessary to filter off all the solid matter in preparing a supersaturated solution.

Limited and Unlimited Solubility. — We have every degree of solubility represented. Many solids are soluble in water to only a very slight extent, while other solids dissolve in much less than their own weight of water. There is no solid known which dissolves in water to an unlimited extent.

Some liquids are scarcely soluble in water at all, while others are miscible with water in all proportions. Thus, the oils are very

slightly soluble in water, while the alcohols are miscible with, or what is the same thing, dissolve in water in all proportions.

Gases show very different degrees of solubility in water. Some are only slightly soluble, while others dissolve in very considerable quantities. For any given gas the solubility varies with the pressure — the greater the pressure the greater the solubility. A simple relation was discovered by Henry connecting the solubility of a gas with the pressure, and which has come to be known as *Henry's Law. The amount of a gas dissolved by a liquid is proportional to the pressure to which the gas is subjected.* Henry's law has stood in general the test of experiment, but there are exceptions known to it, especially when the gas is quite soluble.

No gas is soluble in water to an unlimited extent.

These relations which have been applied to water as a solvent hold also for other liquids.

Properties of Water affected by Dissolved Substances. — Certain properties of the solvent are very greatly affected by dissolved substances. The *freezing-point of water* is lowered by dissolved substances, and this is perfectly general no matter what the nature of the substance which is dissolved in the water. Similarly, the *boiling-point of water* is raised by the presence of substances dissolved in it. Since boiling-point varies inversely as vapor-tension, this is the same as to say that the dissolved substance lowers the vapor-tension of the solvent. This is also a general effect, independent of the nature of the dissolved substance.

The power of *water to conduct the electric current* is also greatly affected by the presence of certain dissolved substances. Pure water is almost a non-conductor of the current. *A cubic millimetre of the purest water which has been thus far prepared, offers the same resistance to the passage of the electric current as a copper wire whose cross-section is one square millimetre, wrapped around the earth one thousand times.* When certain classes of substances are dissolved in water the solution becomes a good conductor, while other substances do not impart this property to water. Those substances whose solutions conduct the current, which we shall learn to know as acids, bases, and salts, are called *electrolytes;* while those substances whose solutions do not conduct the current, including all except the above compounds, are known as *non-electrolytes.*

The Dissociating Power of Water. — The question naturally arises, Why do solutions of some substances conduct the current, and solutions of other substances not conduct? This question is much more easily asked than it is answered. It has been found by elaborate

experimental investigations that all those substances which, when in solution, conduct the current, and only those, produce greater lowering of the freezing-point and greater lowering of the vapor-tension of water than the substances whose solutions do not conduct the current. We shall learn that the amount by which the freezing-point or the vapor-tension of a solvent is lowered, depends only upon the ratio between the number of parts of the solvent and the number of parts of the dissolved substance. If one substance produces a greater lowering of freezing-point or of vapor-tension than another at equal concentration, it means that its solution contains a larger number of parts. From this and other lines of reasoning which will be considered a little later, we are forced to the conclusion that water (and also other solvents) has the power of breaking down the molecules of certain substances which we have called electrolytes into parts. The parts are, however, not simply the atoms, but the atoms or groups of atoms charged with electricity. These charged parts are known as *ions*, and the breaking down of molecules into ions as *dissociation*. Since the ions are the carriers of electricity and separate at the poles in electrolysis, this kind of dissociation is known as *electrolytic dissociation.*

When a molecule is electrolytically dissociated by a solvent like water, one of the ions is always charged positively and the other negatively. The positively charged ion is called the *cation*, and the negatively charged ion the *anion*.

HYDROGEN DIOXIDE

Hydrogen Dioxide. — One compound of hydrogen and oxygen other than water calls for special comment. This is the compound *hydrogen dioxide*, which, as the name implies, contains more oxygen than water. It has the composition expressed by the formula H_2O_2, and is, therefore, an oxidized water. It probably occurs in the atmosphere, but only in very small quantities.

Preparation and Purification. — Hydrogen dioxide is most readily prepared in any quantity by treating a compound with which we had to deal when we were studying oxygen, called barium dioxide, with an acid. If we use hydrochloric acid, the equation is expressed thus: —

$$BaO_2 + 2\,HCl = BaCl_2 + H_2O_2.$$

If we employ sulphuric acid, thus: —

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2.$$

The cold dioxide is introduced slowly into the cold, dilute acid, when the reaction indicated by the equations takes place. In this manner the commercial product is prepared, and this contains about three per cent of the dioxide.

The commercial product nearly always contains a trace of hydrochloric or sulphuric acid. This can best be removed by treating the dioxide with a little zinc oxide, frequently shaking it and allowing it to stand for several hours. The solution of the dioxide is then filtered to remove any excess of the oxide of zinc, and distilled under diminished pressure to free it from any zinc which has dissolved.

If it is desired to prepare a more concentrated solution of hydrogen dioxide, this is effected by slowly evaporating the more dilute, purified solution on a water-bath at a temperature below 75°. Water boils lower than hydrogen dioxide, and under these conditions distils out of the aqueous solution of the dioxide, and for the most part leaves the dioxide behind. The distillation must take place far below the boiling-point of water, since at 100° hydrogen dioxide undergoes marked decomposition. Indeed, some of the dioxide decomposes at 75°, especially if there is any appreciable amount of impurity present. A fairly concentrated solution of the dioxide can be obtained in this manner.

If this solution is now distilled under a pressure of from ten to twenty millimetres of mercury, a fairly pure hydrogen dioxide can be obtained. The object of the diminished pressure is to lower the temperature at which the solution will boil, as we have already seen to be the result in the case of water. The liquid which first passes over is almost pure water, containing only a little of the dioxide, since water boils at all pressures lower than the dioxide. The liquid which comes over later is almost pure hydrogen dioxide.

This process of separating liquids, based upon differences in their boiling-points, is known as *fractional distillation*, and is an important operation in chemistry, as we shall learn.

Properties of Hydrogen Dioxide. — Hydrogen dioxide is a colorless, viscous liquid, much heavier than water, having a specific gravity of 1.4996. We saw that water in thick layers has a markedly bluish tint. Hydrogen dioxide is still deeper blue when observed in thick layers.

One of the characteristic properties of hydrogen dioxide is the ease with which it decomposes into water and oxygen.

$$2\ H_2O_2 = 2\ H_2O + O_2.$$

This is the reason why such precautions have to be taken in purifying it to prevent decomposition.

The concentrated hydrogen dioxide is very explosive, on account of the ease with which the above decomposition takes place. When it is brought in contact with certain solid substances, such as the metals or metal oxides, the decomposition is so rapid that violent explosions result.

Hydrogen Dioxide a Good Oxidizing Agent.—On account of the ease with which hydrogen dioxide gives up oxygen it is a good oxidizing agent. If brought in contact with substances which can take up oxygen it parts with it readily, and such substances are oxidized. Upon this fact is based its value as a *disinfectant.* When brought in contact with organic matter it oxidizes it and destroys its vitality. Bacteria and other germs which produce disease are thus destroyed by hydrogen dioxide.

As an oxidizing agent, it has various applications in the field of chemistry. This property enables it to be readily *detected.* When hydrogen dioxide is brought in contact with a solution of potassium iodide, oxidation takes place, converting the potassium into potassium hydroxide and liberating the iodine.

$$2\,KI + H_2O_2 = 2\,KOH + 2\,I.$$

The iodine is recognized at once by its brown color, or by its power to color starch paste blue.

Hydrogen Dioxide also a Reducing Agent.—We have seen that a reducing agent is one that adds hydrogen to a compound. We must now add that it is also one that removes oxygen from a compound. Hydrogen dioxide has the remarkable property of being not only a good oxidizing agent, as we have just seen, but also of being a good reducing agent in a number of cases. When hydrogen dioxide is brought in contact with metal oxides rich in oxygen, both the dioxide and the metal oxide give up their excess of oxygen. When hydrogen dioxide is brought in contact with manganese dioxide or lead dioxide in the presence of an acid, the following reactions take place:—

$$H_2O_2 + MnO_2 = H_2O + MnO + O_2;$$
$$H_2O_2 + PbO_2 = H_2O + PbO + O_2.$$

It should be observed that exactly one-half of the oxygen set free comes from the hydrogen dioxide and one-half from the oxide of the metal. Each substance being rich in oxygen gives up a part of its oxygen and is reduced; the metal forming the salt of the acid

Catalytic Decomposition of Hydrogen Dioxide. — It was stated above that when fairly concentrated hydrogen dioxide is brought in contact with certain metals like platinum, it is decomposed with explosive violence. Metallic platinum, especially in the finely divided condition, can also decompose dilute hydrogen dioxide. This can be illustrated very readily by simply bringing a piece of platinum sponge, or some platinum black obtained by depositing platinum electrolytically, in contact with hydrogen dioxide. The platinum will become covered at once with a layer of gas, which is oxygen resulting from the decomposition of the dioxide.

Many other metals and certain minerals, such as pyrolusite, effect the same decomposition by simple contact with hydrogen dioxide.

One other characteristic of this reaction should be observed. A very small amount of the solid substance can decompose a large amount of the dioxide, and further, the platinum or other solid is unchanged by the reaction — it does not enter into the reaction.

We have already become acquainted with a similar reaction in the combination of oxygen and hydrogen, as effected by contact with metallic platinum. Such reactions were termed *catalytic.* We have here another example of a catalytic reaction. The platinum does not enter into the reaction, and a small amount decomposes a large amount of the dioxide. These are the conditions which must be fulfilled in order that a reaction may be termed catalytic — in order that we may have catalysis.

Relations of Water and Hydrogen Dioxide. — We have seen that as far as composition is concerned hydrogen dioxide is simply oxidized water. We have also seen that the properties of the two substances are very different. Water is a very stable chemical compound, undergoing decomposition only with the greatest difficulty. To decompose pure water an electric current of high voltage must be used, or it must be subjected to an enormous temperature. Hydrogen dioxide, on the other hand, is a very unstable substance, undergoing decomposition under the slightest provocation, or even spontaneously. The presence of the extra oxygen atom in water has thus apparently changed it from one of the most stable to a very unstable substance.

This is a mere statement of the facts observed, but the reasoning mind is never content to stop here. Why does the presence of one more oxygen atom in water give it such different properties? This is the question which every thinking person must ask. It can never be answered by simply studying the composition of the two sub-

stances — the material side of the problem. We must go deeper into the problem and see what are the energy relations which obtain in the different substances.

When we were studying oxygen and ozone we saw that the latter differed from the former essentially only in the amount of intrinsic energy present in its molecule. In the case of water and hydrogen dioxide we have already discovered a difference in composition. Is there any marked difference in the amounts of energy present in the two molecules? We can answer this question by converting hydrogen dioxide into water and measuring the amount of heat liberated. Suffice it to say here that a *large amount of heat is set free when hydrogen dioxide passes over into water.* This shows that hydrogen dioxide contains more intrinsic energy in the molecule than water, and this is the real cause of the marked difference in properties between the two substances. Hydrogen dioxide containing the larger amount of intrinsic energy is the less stable substance, and this is strictly analogous to what we observed in the comparison of oxygen and ozone. Ozone, containing the larger amount of intrinsic energy in its molecule, is far more unstable than oxygen.

We shall learn that this is a general relation. The more intrinsic energy there is present in a substance, other things being equal, the less its stability. This may be accounted for on the basis of intrinsic energy tending to pass over into heat energy. In order that this may occur, chemical transformation must take place. Indeed, this probably lies very close to the foundation of all chemical reaction.

CHAPTER VI

DETERMINATION OF RELATIVE ATOMIC WEIGHTS

Combining Numbers and Atomic Weights. — We saw in the second chapter that the atomic theory was proposed to account for certain well-established laws of chemical combination — the laws of definite and multiple proportions and of combining weights. If atoms are the ultimate units of matter, these must have definite weights, and it is obviously of great importance for chemistry to determine the relative weights of the atoms of different substances.

If the same number of atoms of any two substances combine, the combining numbers or relative weights of the substances that combine represent the relative weights of the atoms which enter into combination. This apparently furnishes a means of determining relative atomic weights. It is only necessary to determine the relative weights of substances which combine — the combining numbers — in order to ascertain the relative weights of the atoms of these substances. This would be true if a given number of atoms of one substance always combined with an equal number of atoms of another. But we know that this is not the case, since it often happens that two elementary substances combine in several proportions. To determine the relative atomic weights of the elements, we must, therefore, know the combining numbers of the elements, and also the number of atoms of the different elements which combine with one another. We will take up first the method of determining the combining numbers of the elements.

Chemical Methods of determining Combining Numbers. — The simplest method would be to take some element as our standard, and call its combining number one. Then allow all of the other elements to combine with this one, and determine the weights of the different elements which combined with unit weight of our standard element. Since hydrogen has the smallest combining number, it would naturally be chosen as the unit. The problem then would be to determine, say, the number of grams of the different elements which combine with one gram of hydrogen, and these figures would represent the combining weights of the elements in terms of hydrogen as unity. Since it is true that comparatively few of the elements combine

directly with hydrogen, the direct comparison with hydrogen cannot be made in many cases.

A large number of the elements, however, combine directly with oxygen. We can determine the ratio between the combining numbers of these elements and oxygen, and then the ratio between the combining number of oxygen and that of hydrogen, and thus calculate the combining numbers of the elements in terms of our unit hydrogen.

We might thus work out a table of the combining numbers of all of the elements in terms of hydrogen as unity. This part of the problem is, however, not as simple as would be indicated from the above. Many of the elements combine in more than one proportion. Take the case of hydrogen and carbon. The combining number of carbon in terms of hydrogen as unity would be 3, if determined by the analysis of marsh gas. From the analysis of ethylene we would conclude that it was 6, while from the analysis of acetylene it would appear to be 12. A similar complexity would result in the case of carbon and oxygen. If we take oxygen as 16 in terms of hydrogen 1, the combining number of carbon, as determined from carbon monoxide, would be 12, while as determined from carbon dioxide it would be 6. We would thus obtain different combining numbers for the same element, depending upon which of its compounds we selected.

It is perfectly clear that neither the chemical analysis of the compound, nor its synthesis from the elements, throws any light on the problem as to the number of atoms of one substance combined with one atom of the other. Berzelius attempted to solve this part of the problem of atomic weights by means of certain dogmatic rules, which have only this value, that they brought out a large amount of experimental work which resulted in new and improved methods of analysis. Chemical methods alone can lead only to the combining weights or numbers of the elements, and, as already stated, in many cases more than one combining weight for an element would be obtained. Other methods must be employed in order to determine the number of atoms of the one element which have combined with one atom of the other. To these we shall now turn.

Molecular Weights determined from the Densities of Gases. — Gay-Lussac showed in 1808 that the densities of gases are proportional to their combining weights, or to simple rational multiples of them. If two gases react chemically, the volumes which react are either equal, or bear a simple rational relation to one another. And, further, if the product formed is a gas, its volume bears a simple rational relation to the volumes of the gases from which it was

formed. Thus, one volume of hydrogen combines with one volume of chlorine, and forms two volumes of hydrochloric acid gas. One volume of oxygen combines with two volumes of hydrogen, forming two volumes of water-vapor. One volume of nitrogen combines with three volumes of hydrogen, forming two volumes of ammonia.

From the laws of definite and multiple proportions, the law of combining numbers, and the atomic theory which was proposed to account for these, we see that every chemical reaction takes place between a definite number of atoms, and the number is usually small. Therefore, the discovery of Gay-Lussac leads to the conclusion that —

The number of atoms contained in a given volume of any gas must bear a simple, rational relation to the number of atoms contained in an equal volume (at the same temperature and pressure) of any other gas.

We have thus far, however, no means of determining the numerical value of this relation, and, therefore, cannot use the discovery of Gay-Lussac alone to determine relative atomic weights.

Avogadro's Hypothesis. — Avogadro, in 1811, taking into account all of the facts known, advanced the hypothesis that —

In equal volumes of all gases, at the same temperature and pressure, there is an equal number of ultimate parts or molecules.

Avogadro extended his hypothesis to all gases, including even the elementary gases, and regarded the molecules of these substances as made up of atoms of the same kind, which had united with one another. This was a necessary consequence of his hypothesis. One volume of hydrogen gas combines with one volume of chlorine gas, and forms two volumes of hydrochloric acid gas. If there are the same number of molecules in equal volumes of all gases, there would be twice as many in the two volumes of hydrochloric acid as in the one volume of hydrogen, or the one volume of chlorine. Since each molecule of hydrochloric acid must contain at least one atom of hydrogen and one atom of chlorine, the molecule of hydrogen and of chlorine must be made up of at least two atoms. Ampère, in 1814, advanced essentially the same hypothesis as had been proposed three years before by Avogadro. The hypothesis of Avogadro has been confirmed by such an abundance of subsequent work, in so many directions, that it is now placed among the well-established laws of nature. It points out distinctly the difference between atoms and molecules, and rationally explains why different gases should obey the same law of volume and of pressure, and have the

same temperature coefficient of expansion. It has been tested from both the physical and mathematical standpoints, and now lies at the basis of much of our knowledge of gases.

Avogadro's Hypothesis and Molecular Weights. — Given the hypothesis of Avogadro, the determination of the relative molecular weights of gases is very simple. If there is an equal number of molecules contained in equal volumes of the different gases, the relative weights of equal volumes of these gases give at once the relative weights of the molecules contained in them. It is only necessary to choose some substance as our standard, and express the molecular weights of other substances in terms of this standard. We would naturally select as the unit that substance which has the smallest density, and this is hydrogen. From what has been said, however, in reference to the union of hydrogen and chlorine, forming hydrochloric acid, it is certain that the molecule of hydrogen contains at least two atoms. We will, therefore, call the molecular weight of hydrogen two, and calculate the molecular weights of other elements in terms of this standard. The densities of substances are usually determined in terms of air as the unit. It is a simple matter to recalculate these in terms of hydrogen as two. The density of hydrogen in terms of air as the unit is 0.0696. We must multiply this by 28.73 to obtain our new unit 2 ($2 \div 0.0696 = 28.73$). Similarly, for other substances whose densities are known with reference to air; and these densities must be multiplied by the constant 28.73 to transform them into densities in terms of hydrogen = 2. These latter values are the relative molecular weights of the substances in the form of gas, referred to the molecular weight of hydrogen as two. A few results are given in the following table, showing in column I the densities in terms of air as the unit; in column II the densities or relative molecular weights in terms of hydrogen = 2. The results in column II are obtained by multiplying the results in column I by 28.73.

	I		II
Hydrogen, 0° C.	0.0696		2
Oxygen, 0° C.	1.10563		31.76
Nitrogen, 0° C.	0.9713		27.90
Sulphur, 1400° C.	2.17	× 28.73	62.34
Chlorine, 200° C.	2.45		70.38
Bromine, 100° C.	5.54		159.16
Mercury, 1400° C.	6.81		195.65
Iodine, 940° C.	8.72		250.52

The molecular weights of compounds can be determined in exactly the same manner from the densities of their vapors. If these have been determined on the basis of air as unity, we must multiply by 28.73 to obtain the molecular weight referred to hydrogen as two. The molecular weights of compounds, thus obtained, must bear a rational relation to the combining weights of the elements which enter into the compound. The molecular weights as obtained from vapor-densities can, therefore, be corrected by the most careful analytical or synthetical determination of the combining weights of the elements which enter into the compounds.

Atomic Weights from Molecular Weights. — If we knew the number of atoms contained in the molecule of elements in the gaseous state, the problem of relative atomic weights would be solved at once by dividing the molecular weight of the gas by the number of atoms in the molecule. The problem is, however, not as simple as this, since we do not know *a priori* the number of atoms in the molecules of elements. Other lines of thought have enabled us to solve this, the second part of our problem.

The definition of an atom as an indivisible particle of matter shows that fractions of atoms cannot exist. No molecule can contain a fraction of any atom. The quantity of any substance which enters into a molecule must be at least one atom. It may be more than one, but it cannot be less. This is the key to the problem. Suppose we wish to determine the number of hydrogen atoms in a molecule of hydrogen. We must examine compounds into which hydrogen enters, and find out what is the smallest quantity of hydrogen which enters into the molecule of the compound. Let us take hydrochloric acid, whose molecular weight is 36.45. This is shown by analysis to be composed of 1 part of hydrogen and 35.45 parts of chlorine. This 1 part of hydrogen is at least one atom; it may be more, but it cannot be less. By examining a large number of compounds into which hydrogen enters, it has been found that hydrogen never enters into a molecule of any substance in a smaller quantity than in hydrochloric acid. This is, therefore, for us the atom of hydrogen, but it may in reality be composed of a great number of smaller parts. The hydrogen which enters into the molecule of hydrochloric acid is just half the quantity which forms the molecule of hydrogen gas, since one volume of hydrogen combining with one volume of chlorine yields two volumes of hydrochloric acid gas. The molecule of hydrogen, therefore, contains at least two atoms, and since there is no experimental reason for assuming that it contains more than two, we say that the molecule

of hydrogen is made up by the union of two hydrogen atoms. Knowing the number of atoms in the molecule, the atomic weight follows at once from the molecular weight determined by vapor-density, and corrected by the most refined methods of chemical analysis.

By methods similar to the above the molecules of many elements have been shown to be composed of two atoms. But this by no means applies to all elementary substances. The molecules of some elementary substances contain more than two atoms, and in a very few cases the molecule and atom seem to be identical. And, further, the number of atoms contained in the molecule has been shown to vary in some cases with change in conditions, especially with change of temperature. But by studying a large number of compounds of an element, and ascertaining what is the smallest quantity of the element which ever enters into a compound, we can determine the number of atoms contained in a molecule of the element itself. Knowing the number of atoms in the molecule of the element, and the weight of the molecule, we can determine relative atomic weights. The relations between the molecular weights of a few of the elements and their atomic weights are given in the following table: —

Elements	Atomic Weights	Molecular Weights
Hydrogen	1	2
Nitrogen	14.01	28.02
Oxygen	15.88	31.76
Phosphorus	30.96	123.84
Sulphur	31.98	{ 63.96 above 800° C. 191.88 at 500° C.
Chlorine	35.18	70.36
Arsenic	74.9	299.6
Selenium	78.9	157.8
Bromine	79.34	158.68
Cadmium	111.7	111.7
Tellurium	126.3	252.6
Iodine	125.89	251.78 under 600° C.
Mercury	199.8	199.8

This table brings out a number of facts to which reference has already been made. The molecular weight of a number of the elements is twice as great as the atomic weight. In some cases, as with sulphur, the molecular weight is twice the atomic weight at a given temperature, and then varies with the temperature. In the

cases of cadmium and mercury the molecular weights are apparently identical with the atomic weights. This matter will be taken up later in other connections.

It frequently happens that an element boils at such a high temperature that we cannot determine accurately its vapor-density. In such cases volatile compounds of the element are used, and their molecular weights determined. These compounds are then analyzed, and the one containing the smallest quantity of the given element in its molecule is said to contain one atom of the element. The real atom of the element may be a fraction of this quantity, but this is for all chemical or physical chemical purposes the atom, and its relative weight is the atomic weight of the element in question.

Atomic Weights from Specific Heats. — Dulong and Petit in 1819 showed that a very simple relation exists between the specific heats of elements in the solid state and their atomic weights. They found that the specific heats varied inversely as the atomic weights, and, consequently, that the product of the specific heats and atomic weights of the elements is a constant. This will be seen from the following data: —

	Specific Heat	Atomic Weight	Product
Lithium	0.941	7.01	6.6
Sodium	0.293	22.99	6.7
Magnesium	0.250	23.94	6.0
Potassium	0.166	39.03	6.5
Calcium	0.170	39.91	6.8
Iron	0.112	55.90	6.3
Cobalt	0.107	58.60	6.3
Nickel	0.108	58.60	6.4
Zinc	0.0932	64.90	6.1

From these and similar facts Dulong and Petit announced their law: —

The atoms of all elements have the same capacity for heat energy.

After the discovery of this law it was a comparatively simple matter to determine the atomic weights of solid elements from their specific heats. If specific heat multiplied by atomic weight is a constant, the atomic weight is equal to the constant divided by the specific heat. The numerical value of the constant, taken as the average for a number of elements, is about 6.25.

Exceptions to the law of Dulong and Petit were early recognized. Weber determined the specific heats of the elements carbon, boron, and silicon, at temperatures between 0° and 100° C., and obtained much smaller values than would be expected from the law of Dulong and Petit, using the atomic weights of these elements as determined from Avogadro's law. He found, however, that the specific heats of these elements varied widely with change in temperature, and that above a certain temperature the specific heats became constant. At these elevated temperatures, where the specific heats became constant, they conformed to the law of Dulong and Petit. These constant specific heats were obtained only at comparatively high temperatures; for silicon at about 200° C., for the different modifications of carbon at about 600° C., for boron at about 500° C. The different modifications of carbon had different specific heats at low temperatures, but at elevated temperatures this difference also was found to vanish, the different varieties of carbon at red heat showing the same specific heats. Similar observations were made on glucinum by Nilson and Pettersson.

The law of Dulong and Petit is, in general, only approximately true, and holds only within certain limits of temperature.

The relation between the specific heats of compounds and the specific heats of their constituents was next investigated. Neumann showed that equivalent quantities of analogous compounds have the same capacity for heat, and Regnault, Kopp, and others pointed out the following relation between the specific heats of compounds and the specific heats of their constituents. *The capacity of the atoms for heat energy is not appreciably changed when they unite and form compounds.* In a word, the capacity of the molecule for heat is the sum of the capacities of the atoms in the molecule.

The recognition of this relation makes it possible to greatly extend the method of determining atomic weights by specific heats. Many of the elements are solids only at temperatures which are too low to be dealt with by the methods of measuring specific heats. But these elements form solid compounds with other elements whose specific heats and atomic weights can be determined. Let us take an example.

Chlorine is an element whose specific heat in the solid state would be very difficult to determine. Chlorine, however, forms a solid compound with the element lead. The specific heat of lead chloride has been found by Regnault to be 0.0664; 206.4 parts of lead yield 277.1 parts of lead chloride. Multiplying this number by the spe-

cific heat of lead chloride, we obtain the molecular heat. $277.1 \times 0.0664 = 18.4$. Subtracting the atomic heat of lead, 6.5, we have 11.9 as the atomic heat, corresponding to 70.7 parts of chlorine. Since the atomic heat of the elements is about 6, we have in 70.7 twice the atomic weight of chlorine, or the atomic weight of chlorine = 35.35. This agrees very closely with the atomic weight of chlorine determined by the vapor-density method, based upon the law of Avogadro, and by analysis.

The above example serves to illustrate the way in which the specific heats of compounds are used to determine atomic weights. The method has been widely applied, and it may be said in general, that the atomic weights determined from the law of Dulong and Petit agree with those obtained from the law of Avogadro, although some discrepancies exist.

Isomorphism an Aid in determining Atomic Weights. — It was recognized even in the eighteenth century that substances of different composition often have the same, or very nearly the same crystal form. This was at first explained by assuming that certain substances have the power of forcing other substances to take their own crystal form. Mitscherlich interpreted this fact quite differently. He studied the salts of arsenic and phosphoric acids, and found that those which contained an equal number of atoms in the molecule had the same, or very similar crystal forms. Mitscherlich concluded at first that it was only the number and not the nature of the atom which conditioned the crystal form. Later, he recognized that the way in which the atoms were united in the compound was an important factor in determining its crystal form, and then arrived at the generalization that, "*An equal number of atoms combined in the same way produce the same crystal form, and that the same crystal form is independent of the chemical nature of the atoms, but depends only on their number and position.*"

If this relation was true, it would throw much light on the number of atoms in a compound, and, therefore, be of service in determining atomic weights. Given two isomorphous substances such as $BaCl_2\ 2\ H_2O$ and $BaBr_2\ 2\ H_2O$; from the law of Mitscherlich their molecules must contain the same number of atoms. If we know the atomic weights of all the elements in the former compound, we can find the atomic weight of the bromine in the latter substance.

This relation pointed out by Mitscherlich was accepted at once by Berzelius, who made it the basis of atomic weight determinations. The law, however, did not long remain without exceptions.

Mitscherlich showed that the compounds $BaMn_2O_8$, Na_2SO_4, and Na_2SeO_4 are isomorphous, and they evidently contain a very different number of atoms in the molecule. An attempt was made to overcome this difficulty by ascribing to these compounds the formulas, $BaMn_2O_8$, NaS_2O_8, and $NaSe_2O_8$, but these were so strongly at variance with all the facts known that they had to be abandoned, and a number of other substances were soon discovered to be isomorphous which could not possibly be regarded as containing the same number of atoms in the molecules.

The generalization of Mitscherlich is then only an approximation to which there are many exceptions, and this method of determining atomic weights must be used with great caution.

The modifications of the law of Mitscherlich proposed by Marignac and Kopp have scarcely increased our confidence in it as a means of determining atomic weights. The former has shown that equality in the number of atoms in compounds is not necessary in order that we may have isomorphism, and Kopp would limit the term isomorphism to substances which will grow in each other's solutions. The application of the conception of isomorphism to the problem of atomic weights has, however, been of much service, especially in the earlier stages of such work.

Most Accurate Method of determining Atomic Weights. — The general methods described for determining the relative atomic weights of the elements differ greatly in their relative accuracy. Of these the various chemical methods for determining the constituents of compounds are by far the most accurate. Indeed, the other methods described, such as the vapor-density method, and the methods based upon specific heat of solids, and upon isomorphism, must be regarded simply as checks upon the chemical methods. By means of chemical analysis or synthesis, we determine with the greatest degree of accuracy the combining weights of elements, and then make use of the other methods to decide whether we are dealing with one or more atoms.

In determining atomic weights we must choose some element as our standard. We would naturally take the lightest element, hydrogen, and call it unity. This has been done, and all atomic weights referred to this unit. But it is unfortunately true, as has been stated, that hydrogen does not combine directly with many of the elements and form stable compounds which can be analyzed.

Oxygen, on the other hand, does combine with a large number of the elements, forming some of the most stable compounds with which

we are acquainted. It therefore seemed best to compare the atomic weights of the elements directly with the atomic weight of oxygen, and then compare oxygen with hydrogen, with which it forms the very stable compound, water. It should be stated, however, that this method is by no means free from objections, and many prefer retaining hydrogen as the unit. The atomic weight of oxygen, in terms of hydrogen as the unit, was supposed for a long time to be the whole number 16. If this was true, it would obviously make no difference whether we called hydrogen 1 or oxygen 16, and then compare all other atomic weights with these standards. It has recently been shown beyond question that when hydrogen is 1, oxygen is not 16, but considerably less (15.88). We must, therefore, choose between these two substances as the basis of the system of atomic weights. The majority of investigators at present seem inclined to select oxygen as the standard, taking its atomic weight as 16, and referring the atomic weights of all the other elements to this basis.

The most direct method of determining the combining weight of an element, in terms of oxygen as our standard, would be to determine the weight of the element which would combine with a known weight of oxygen. The combining weight of the element would then be calculated by the simple proportion, —

Wt. oxygen : wt. element = at. wt. oxygen : combining wt. element.

We should then have to determine, by some of the methods already referred to, how many atoms of the element in question combined with one atom of oxygen.

While it is true that oxygen combines directly with many of the elements, forming stable compounds, it is by no means true that it forms such compounds with all of the elements. And further, some of the elements form compounds with oxygen which are gaseous or liquid at ordinary temperatures, and for these or other reasons are not adapted to atomic weight determinations. In such cases the atomic weight of the element must be compared with that of some element other than oxygen, which in turn has been compared with oxygen. Thus, the atomic weights of the halogens have been determined in terms of the atomic weight of silver, and the latter then determined in terms of oxygen. Even more complex cases may arise, where it is necessary to compare the atomic weight of an element with the sum of the atomic weights of two or more elements, each of which has been determined in terms of oxygen.

It is evident that the more direct the comparison of the atomic

weight of the element with that of oxygen, the better; since the accumulation of experimental errors, resulting from indirect comparisons, is avoided.

Some of the most refined experimental work which has ever been done has had to do with the problem of relative atomic weights. It is obviously necessary that these constants should be determined with the very greatest degree of accuracy, since all chemical analysis and much of the most refined work in physical chemistry and in physics depends upon them. In this connection we should mention, especially among the earlier work, that of Stas and Marignac, and among the more recent investigations those of Morley and Richards.

The work of Stas had to do more especially with the relations between silver and the halogens, but included, also, a large number of other elements, especially lithium, sodium, potassium, sulphur, lead, and nitrogen. The work of Stas, as a whole, has become a model for refinement and accuracy, and is simply wonderful, when we consider the comparatively crude apparatus with which it was carried out.

Marignac has done an enormous amount of work on the problem of atomic weights. He has determined the atomic weights not only of chlorine, bromine, and iodine, but of carbon and nitrogen, calcium, barium, magnesium, zinc, manganese, nickel, cobalt, lead, bismuth, and many of the rarer elements.

The comparatively recent work of Morley on the ratio between the atomic weights of oxygen and hydrogen is one of the finest pieces of scientific work in modern times. He has established this ratio by different methods, with an unusual concordance in the results, to be 1 : 15.879.

The work of T. W. Richards on the atomic weights of a large number of the metals should receive special mention. He has improved old methods, devised new ones, and applied them with a skill which is rare. His determinations are to be ranked among the very best which have ever been made.

Table of Atomic Weights. — The most probable atomic weights of the elements, based upon the best determinations, are given in the following table. In preparing this table the tables of Clarke, of Richards, and of the committee of the German Chemical Society have all been carefully considered; also the original determinations themselves, wherever there were appreciable differences between the values chosen by the different authorities. The basis of this table is oxygen = 16.

Element	Atomic Weight	Element	Atomic Weight
Aluminium	27.1	Neodymium	143.6
Antimony	120.2	Neon	20.0
Argon	39.9	Nickel	58.7
Arsenic	75.0	Nitrogen	14.04
Barium	137.4	Osmium	191.0
Bismuth	208.5	Oxygen	16.0
Boron	11.0	Palladium	106.5
Bromine	79.96	Phosphorus	31.0
Cadmium	112.4	Platinum	194.8
Cæsium	132.9	Potassium	39.15
Calcium	40.1	Praseodymium	140.5
Carbon	12.0	Radium	225.0 (?)
Cerium	140.25	Rhodium	103.0
Chlorine	35.45	Rubidium	85.5
Chromium	52.1	Ruthenium	101.7
Cobalt	59.0	Samarium	150.3
Columbium	94.0	Scandium	44.1
Copper	63.6	Selenium	79.2
Erbium	166.0	Silicon	28 4
Fluorine	19.0	Silver	107.93
Gadolinium	156.0	Sodium	23 05
Gallium	70.0	Strontium	87 6
Germanium	72.5	Sulphur	32.06
Glucinum	9.1	Tantalum	183.0
Gold	197.2	Tellurium	127.6
Helium	4.0	Terbium	160.0
Hydrogen	1.008	Thallium	204.1
Indium	115.0	Thorium	232.5
Iodine	126 97	Thulium	171.0 (?)
Iridium	193.0	Tin	119.0
Iron	55.9	Titanium	48.1
Krypton	81.8	Tungsten	184.0
Lanthanum	138.9	Uranium	238.5
Lead	206.9	Vanadium	51.2
Lithium	7.03	Xenon	128.0
Magnesium	24.36	Ytterbium	173.0
Manganese	55.0	Yttrium	89.0
Mercury	200 0	Zinc	65.4
Molybdenum	96.0	Zirconium	90.6

CHAPTER VII

DETERMINATION OF THE MOLECULAR WEIGHTS OF GASES AND OF DISSOLVED SUBSTANCES

DENSITIES AND MOLECULAR WEIGHTS OF GASES

Densities and Molecular Weights. — The determination of the relative densities of gases consists in determining the relative weights of equal volumes of gases at the same temperature and pressure. Since equal volumes of gases under the same conditions contain an equal number of molecules, the densities stand in the same relation as the molecular weights. Thus, by means of Avogadro's law we can determine the molecular weights of substances in the gaseous state.

Some substance must be taken as the unit in determining the densities in gases. Air has generally been selected as the unit, and the weights of equal volumes of other gases, at the same temperature and pressure, compared with that of air. Hydrogen has also been used as the unit, and is to be preferred to air, since the composition of the latter varies slightly from time to time and from place to place. The density of air is 14.37 times the density of hydrogen, and since the molecular weight of hydrogen is 2, we must multiply the density referred to air as the unit by 28.73 to obtain the molecular weight of the gas. If we represent the molecular weight of the gas by m, and the density referred to air as the unit by d,

$$m = d \times 28.73.$$

In this way the molecular weights of gases can be calculated from their densities.

A number of methods, and a large number of modifications of methods have been proposed for determining the densities of gases. The more important will be briefly considered.

Method of Dumas. — The method of Dumas consists in determining the amount of substance which, in the form of vapor, at a given temperature, just fills a flask whose volume is afterwards

determined. The flask is weighed full of air. Knowing the volume of the flask, we know the weight of air contained in it; therefore, we know the weight of the empty flask. The weight of the flask being known, and the weight of the flask plus the substance which just filled it with vapor, we know the weight of the substance. By determining the weights of the vapors of different substances which fill a flask of given volume, we have the relative densities of the vapors.

The apparatus used is a balloon flask (Fig. 12) holding from 100 to 250 cc.

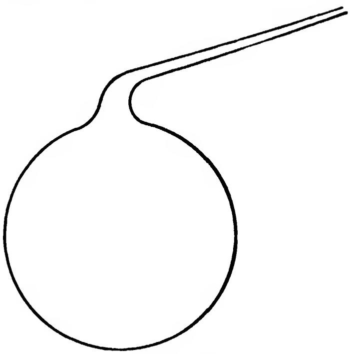


Fig. 12.

The flask is carefully dried and weighed, using as a tare another flask of very nearly the same size. We are in this way made independent of the conditions of temperature, moisture, etc., under which the weighing is made.

A few grams of the substance whose vapor-density is to be determined are introduced into the flask, the neck drawn out to a capillary, and the flask placed in a bath which is at least ten or fifteen degrees above the boiling-point of the substance. The substance vaporizes, drives out the air, and when the vapor of the substance ceases to escape, the capillary is fused shut. The flask after cooling is weighed. The fine point is then cut off under mercury and the flask filled with mercury. The flask may then be weighed again, or the mercury poured out and measured, giving the volume of the flask.

The method of Dumas is not as well adapted to higher temperatures as other methods to be considered later. In the first place, it is difficult to measure high temperatures accurately; and, further, the amount of substance contained in the bulb at high temperatures is so small that relatively large errors result from this source. Deville and Troost have used this method at fairly high temperatures, employing porcelain balloons, but their results are not very accurate. The method of Dumas cannot be used with even a fair degree of accuracy above 600° to 700° C.

An attempt has been made to use the Dumas method under diminished pressure. Habermann has so arranged the bulb that a low pressure can be maintained constant, and the pressure read on a manometer. Larger bulbs are required for work under diminished

pressure, and even then the quantity of substance is so small that considerable errors are introduced.

A large number of modifications of the method of Dumas have been proposed, but that of Bunsen should be especially mentioned. He used three vessels of the same volume and weight. One was empty, one was filled with air at a given temperature and pressure, and the third was filled with the vapor at the same temperature and pressure. If we represent by W_1 the weight of the vessel filled with the vapor, by W_2 the weight of the vessel filled with air, and by W_3 the weight of the vessel in which there is a vacuum, the relative density of the vapor and air is expressed thus: —

$$\frac{W_1 - W_3}{W_2 - W_3}.$$

After vessels of the same volume and weight have once been prepared, this method of procedure is more convenient and far more rapid than that originally described by Dumas.

The method of Dumas is used less to-day than it was formerly, having been largely supplanted by better methods, especially at elevated temperatures. The apparatus used in this method is, however, exceedingly simple, and even at present the Dumas method is employed in certain cases where the presence of a foreign gas in the vapor must be avoided.

The Method of Gay-Lussac. — The method devised by Gay-Lussac for determining the densities of vapors is based upon a principle which is quite different from that which we have just considered. In the method of Dumas the vapor required to fill a given volume was weighed. In the method of Gay-Lussac a weighed amount of substance is converted into vapor, and the volume of the vapor measured. The method as originally proposed by Gay-Lussac consists in placing a known weight of liquid in a calibrated vessel over mercury. The whole is then warmed until the liquid is converted into vapor. The temperature is noted, also the volume of the vapor. The latter is reduced to standard conditions, a correction being introduced for the tension of the mercury vapor. This method has been so greatly improved that the original is no longer used.

Hofmann's Modification of the Gay-Lussac Method. — The modification of the Gay-Lussac apparatus proposed by Hofmann, consists in elongating the inner tube beyond the barometric height so that a vacuum will exist in the top of the tube. The substance is introduced into the tube over the mercury and volatilized under diminished pressure. The apparatus is shown in Fig. 13.

The calibrated tube *A* rests in a mercury reservoir *R*, and is more than 76 cm. long. It is fastened into a vapor-jacket *J*, into which vapor enters at *a*, and leaves at *b*. *m* is a bar of metal terminating in an adjustable point, which is brought down to the surface of the mercury; the cross-hairs attached to the bar at *h* serving to read more accurately the height of the mercury in the tube *A*.

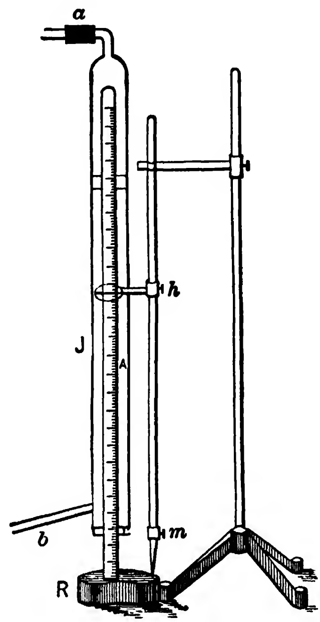


FIG. 13.

After the substance is converted into vapor the volume of the vapor is read and reduced to standard conditions. Knowing the weight of the substance and the volume of vapor, the density of the vapor is calculated at once. The advantage of the modification proposed by Hofmann is that the substance is converted into vapor at a temperature below its boiling-point under atmospheric pressure. Thus, the vapor-density of many substances which would decompose if boiled under atmospheric pressure can be determined. Indeed, Hofmann devised this method especially for use with organic substances which would easily decompose.

The Gas-displacement Method of Victor Meyer. — A method for determining vapor-densities which has practically supplanted all other methods, except in very special cases, was devised by Victor Meyer in 1878. The method consists in volatilizing a small, weighed portion of substance in a tube filled with air, and collecting and measuring the volume of air which is displaced.

The apparatus used is seen in Fig. 14. The inner vessel *A* is surrounded by a glass jacket *J*, in which is boiled some substance which will heat *A* to a constant temperature, and at the same time to the temperature desired. The tube *A* is closed above with a stopper, and from the central tube a side tube runs over to, and under a calibrated tube filled with water and dipping into a water reservoir. The substance to be used is weighed in a weighing tube which is closed loosely at the top, and introduced, when desired, into the top of *A*. In carrying out a determination, a liquid which has a higher boiling-point than the substance whose vapor-density is

to be determined is placed in the outer jacket. This liquid is boiled, and a part of the air in the inner vessel is driven out. When no more air escapes from the side-tube, the tube containing a weighed amount of substance is introduced into the top of A, and rests on the rod r. When temperature equilibrium has been perfectly established, the mouth of the side-tube is placed under the measuring tube in the water tank, the rod r drawn back, and the small vessel containing a weighed amount of the substance allowed to drop to the bottom of A. The substance volatilizes, drives out the loosely fitting cork from the weighing tube, and then displaces air from the tube A. The displaced air is received in the measuring tube t, and its volume is equal to the volume of vapor formed in the tube A by the known weight of the substance introduced. We know the amount of substance used, also the volume of the air displaced, which is equal to the volume of vapor formed; consequently, the density of the vapor of the substance.

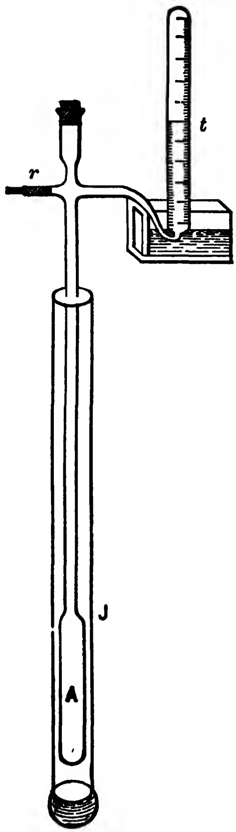


FIG. 14.

A very small amount of substance suffices for determining vapor-density by this method, and the method can be used at very high temperatures. At higher temperatures vessels of glass cannot of course be employed, but porcelain can be used. Berlin porcelain can be employed up to 1600°, and other more resistant forms of porcelain can be used up to 1700°, or perhaps a little higher. Platinum vessels can be used up to 1700°. There is no material known which can be used above 1800°.

The great advantage of this method, in addition to the small amount of substance required, is that the temperature of the experiment does not need to be known. It is only necessary to keep the temperature constant before and after the introduction of the substance. The gas-displacement method is so far superior to all others at high temperatures that it has practically supplanted them all.

It is not necessary to fill the vessel A with air. This may be replaced by an indifferent gas, in case the oxygen of the air would act chemically upon the substance to be vaporized. Thus, if we

were determining the vapor-density of arsenic or sulphur, oxygen must be excluded, and the vaporizing vessel could be filled with nitrogen or hydrogen. If the vapor of magnesium was being studied, nitrogen could not be used, since it would act chemically upon the magnesium.

The gas-displacement method of Victor Meyer has also been used under diminished pressure, and the vapor-densities of substances determined considerably below their boiling-points. The advantage of increased stability of the substance at the lower temperature has already been mentioned.

Method of Bunsen. — Bunsen has devised a rough method of determining the relative densities of gases. Gases under the same pressure pass through a small opening with velocities which are inversely as the square roots of their densities. The method consists in allowing equal volumes of different gases to pass through a very fine hole in a platinum plate, which covers the top of the cylinder containing the gas, and noting the time required. The cylinder is immersed in mercury, which enters from below as the gas escapes at the top. The method is not capable of any very great refinement, and the results obtained by means of it are only close approximations.

Of the methods considered for determining the densities of vapors, that of Meyer is by far the most generally applicable. The method of Gay-Lussac and the modification proposed by Hofmann are seldom used. The method of Dumas is used at present only in special cases, to which reference will be made in detail a little later.

Results of Vapor-density Measurements. — The vapor-densities of elementary gases have shown many interesting and surprising relations between the number of atoms contained in the molecules of these substances. The molecular weights of a number of elementary gases, calculated from their densities, show that the molecule is made up of two atoms. This applies to hydrogen, oxygen, nitrogen, chlorine, bromine, and a number of others. The vapor-densities of mercury, cadmium, and glucinum show that the molecule is monatomic, or that the molecule and atom are identical. On the other hand, the molecules of phosphorus, sulphur, etc., contain more than two atoms, if the temperature to which they are heated is not too high.

Abnormal Vapor-densities. Apparent Exceptions to the Law of Avogadro. — The vapor-densities of the elementary substances mentioned above show that the molecules of some vapors contain a number of atoms, the molecules of others two atoms, while in some vapors at low temperatures, and in others at higher temperatures,

the molecule contains one atom, or the molecular weight is identical with the atomic weight. In the case of no elementary substance, however, was the molecular weight found from vapor-density less than the atomic weight of the element, and in none of the compounds thus far mentioned was the molecular weight less than the sum of the atomic weights of the elements entering into the compound. In a number of cases the molecular weights showed that the molecule of the compound was the simplest possible, but there was nothing to indicate that the simplest molecule had in any case broken down into its constituents. We must now turn to another class of phenomena. The molecular weights of substances like ammonium chloride, phosphorus pentachloride, etc., calculated from their vapor-densities, were less than the sum of the atomic weights of their constituent elements. Thus, the vapor-density of ammonium chloride, corresponding to the formula NH_4Cl, must be 1.89, while Bineau found the value 0.89. The vapor-density of phosphorus pentachloride of the formula PCl_5 must be 7.20. Neumann found by the method of Dumas at 182° the value 5.08. This decreased with rise in temperature up to 290°, where it became constant at 3.7. Similar results were found by Cahours. A number of other examples similar to the above were known, but these suffice to illustrate the point. The explanation of these abnormal results was not furnished at once, and for a time the hypothesis of Avogadro was rather at a discount because of their existence. The explanation, however, has been furnished, as we shall now see, and the law of Avogadro thoroughly substantiated.

Explanation of the Abnormal Vapor-densities. — After Deville had shown in 1857 that many chemical compounds are broken down or dissociated by heat, it occurred to Cannizzaro, Kopp, and others, that the abnormal vapor-densities of substances like ammonium chloride, phosphorus pentachloride, etc., might be due to the dissociation of these substances by heat. If a substance like ammonium chloride was dissociated, one molecule would yield one molecule of ammonia and one of hydrochloric acid. One molecule of phosphorus pentachloride would break down into one molecule of phosphorus trichloride and one molecule of chlorine. If such a dissociation did take place, it would account for the abnormally small vapor-densities found, since the substances in the form of vapor would occupy a greater space than if there was no dissociation. But this did not prove that such a dissociation actually took place. How could this point be tested?

Take the case of ammonium chloride; if it is dissociated by heat

it would yield ammonia and hydrochloric acid in equivalent quantities. It would, however, be exceedingly difficult, if not impossible, to detect either ammonia or hydrochloric acid when the two gases were mixed in equivalent quantities. This problem was solved by Pebal. He made use of the different rates at which these two gases diffuse to separate them, in part, in case they were present in the vapor of ammonium chloride. The apparatus which he used is seen in Fig. 15. The ammonium chloride *d* rests on a plug of asbestos *c*, near the top of the inner tube, which is open above. A stream of hydrogen is passed through *a* into the outer part of the apparatus, and another stream through *b* into the inner part of the apparatus. The whole is heated above the boiling-point of ammonium chloride. If the salt is decomposed when it volatilizes, the ammonia being lighter than the hydrochloric acid would diffuse more rapidly through the plug of asbestos. The vapor in the inner tube below the plug would therefore contain an excess of ammonia. This vapor is swept out by means of the stream of hydrogen gas, and made to pass over a piece of moist, red litmus paper in the vessel *B*. It was found that this was colored blue, proving the presence of an excess of ammonia.

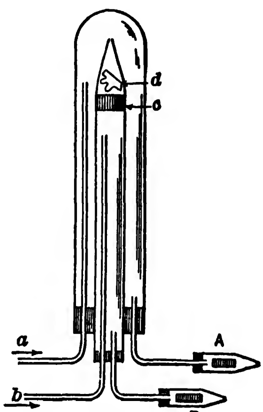


FIG. 15.

The vapor remaining in the inner tube above the wad of asbestos must contain an excess of hydrochloric acid, since more ammonia has passed through the asbestos than hydrochloric acid. This is swept out by means of the stream of hydrogen in the outer vessel, and passed over a piece of blue litmus in the vessel *A*. This turned red at once, showing the presence of free hydrochloric acid in this gas. It would seem, then, that Pebal had demonstrated beyond doubt that the vapor of ammonium chloride contains both free ammonia and free hydrochloric acid, and, therefore, that this substance is dissociated by heat.

The objection was, however, raised to the experiment of Pebal, that a foreign substance, asbestos, had been used in contact with the vapor of ammonium chloride, and that this might have caused the vapor to dissociate, or at least might have facilitated the breaking down of the salt by heat. This objection, while apparently having but little foundation, could not be ignored. To test this point Than

devised the following apparatus (Fig. 16): The tube *AB*, in which the ammonium chloride is contained, is placed horizontally, and the septum is made out of ammonium chloride. Nitrogen is passed through the tube, the ammonium chloride *d* heated with a lamp, and the vapors in the two sides passed over colored litmus, as in the experiment of Pebal. The vapor in the side next to the ammonium chloride was found to contain free hydrochloric acid, and free ammonia was shown to be present in the vapor which had diffused through the plug of ammonium chloride.

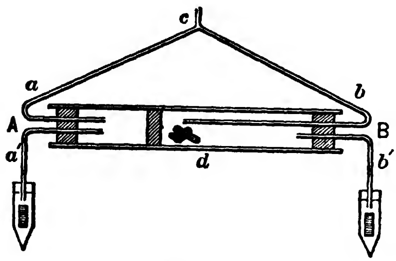


FIG. 16.

It is thus shown beyond question that the vapor of ammonium chloride is broken down, in part, into ammonia and hydrochloric acid, by heat alone.

The work of Wanklyn and Robinson has shown that phosphorus pentachloride is dissociated by heat into the trichloride and chlorine. The pentachloride was placed in a short-necked glass flask, in which it was to be converted into vapor. Over the neck of this flask a wider glass tube was placed, so that the two were separated by an air-space. Air was passed in through the upper tube and escaped through the space between the two glass tubes. If the vapor of the pentachloride was dissociated by heat into the trichloride and chlorine, these would diffuse with different velocities into the upper portion of the vessel, since they have different vapor-densities. They would then be swept out by the current of air in different quantities, the chlorine being in excess since it is the lighter, and would, therefore, diffuse more rapidly into the upper portion of the vessel.

Free chlorine was proved to be present in the vapors which escaped, and analysis showed an excess of phosphorus trichloride remaining in the flask. Therefore, the phosphorus pentachloride was broken down, in part at least, by heat into its constituents. This conclusion was confirmed by the observation that as the vapor of phosphorus pentachloride is heated higher and higher it becomes colored more deeply greenish-yellow,—the characteristic color of chlorine itself.

The same explanation undoubtedly applies to other substances whose vapor-densities are abnormally small. They are more or less

broken down by heat into their constituents; the amount of the dissociation increasing with the temperature.

Dissociation of Vapors diminished by an Excess of One of the Products of Dissociation. — A discovery was made in connection with the study of dissociating vapors, which has proved to be of the very highest importance. If there is present an excess of either of the products of dissociation, the amount of the substance decomposed is lessened. Thus, ammonium chloride is less dissociated if there is present an excess of either ammonia or hydrochloric acid. Similarly, phosphorus pentachloride is much less decomposed at a given temperature if there is present an excess of either phosphorus trichloride or chlorine, as Würtz has shown. Indeed, the vapor of phosphorus pentachloride is scarcely dissociated at all by heat in the presence of an atmosphere of phosphorus trichloride, or of chlorine. The vapor-density of phosphorus pentachloride in an atmosphere of the trichloride was found to be about 209, while the calculated vapor-density is 208.

This is a perfectly general principle, illustrated by phosphorus pentachloride and ammonium chloride. The dissociation of substances in general by heat is driven back by an excess of any one of the products of dissociation.

This is the second example thus far met with of the effect of mass on chemical activity. The importance of the action of mass will be more clearly seen as the subject develops. We shall now take up the law of mass action.

THE LAW OF MASS ACTION

The Work of Guldberg and Waage. — Guldberg, who was later professor of applied mathematics at the University of Christiania, and Waage, professor of chemistry at the same institution, were the first to mathematically formulate the effect of mass on chemical activity. Their first preliminary paper was published in Norwegian in 1864. Their epoch-making paper appeared in 1867. In the first part of their paper they review the theories of affinity which had been held. The views of Bergmann and Berthollet are taken up, and it is pointed out that neither is sufficient to account for all the facts known. They attributed this to the lack of a suitable method for determining the magnitude of affinity. They point out that the method of Bergmann, based on the assumption that if the substance B replaces C from a compound with A, giving the compound AB, the affinity between A and B is greater than between B and C, is not

satisfactory, since this assumption leaves out of account a large number of conditions which affect the reaction. The attempt to measure the magnitude of chemical affinity by the heat evolved during the reaction was regarded as unsatisfactory, because it depends in part upon the conditions under which the reaction takes place.

Guldberg and Waage point out that in chemistry, as in mechanics, we must study forces by their effects, and the most natural method is to determine forces in the condition of equilibrium; "that is to say, we must study the chemical reactions in which the forces which produce new compounds are held in equilibrium by other forces. This is the case in the chemical reactions where the reaction is not complete but partial, *i.e.* in the reactions where —

"(*a*) Addition and decomposition take place at the same time, and where,

"(*b*) Substitution and reformation proceed simultaneously."

The authors do not take up in this paper the case of addition and decomposition, or dissociation, since the data available are not sufficient, but develop the law of mass action from a study of the second class of reactions, viz. substitution.

In the development of the law their own words are given: —

"Let us assume that two substances, A and B, are transformed by double substitution into two new substances, A' and B'; and under the same conditions A' and B' can transform themselves into A and B. Neither the formation of A' and B' nor the reformation of A and B are complete, and at the end of the reaction we have the four substances present A, B, A', and B'. The force which causes the formation of A' and B' is in equilibrium with that which causes the formation of A and B. The force which causes the formation of A' and B' increases proportional to the affinity coefficients of the reaction $A + B = A' + B'$, but it depends also on the masses of A and B.

"We have learned from our experiments that, *the force is proportional to the product of the active masses of the two substances A and B.*

"If we designate the active masses of A and B by p and q, and the affinity coefficient by K, the force $= K . p . q$.

"As we have often observed, the force Kpq, or the force between A and B, is not the only force which comes into play during the reaction. Other forces tend to retard or accelerate the formation of A' and B'. Let us, however, assume that other forces do not exist, and let us see what formula is developed in this case. We believe that the consideration of this ideal reaction, where only the forces

between A and B, and between A' and B' are taken into account, will furnish the reader with a clear and distinct presentation of our theory.

"Let the active masses of A' and B' be p' and q', and the affinity coefficient of the reaction $A' + B' = A + B$, be K'; the force of the reformation of A and B is equal to $K'p'q'$. This force is in equilibrium with the first force, consequently, —

$$Kpq = K'p'q'. \tag{1}$$

"By determining experimentally the active masses p, q, p', and q', we can find the relation between the affinity coefficients K and K'. On the other hand, if we have found this relation $\frac{K'}{K}$, we can calculate the result of the reaction for any original condition of the four substances."

MOLECULAR WEIGHTS OF DISSOLVED SUBSTANCES

Determination of the Molecular Weights of Dissolved Substances by the Freezing-point Method. — We have already learned that the freezing-point of water is lowered by the presence of dissolved substances. The amount of the lowering has been shown by the French physical chemist Raoult, to be proportional to the ratio between the number of molecules of the solvent and the number of molecules of the dissolved substance. If we know the lowering of the freezing-point of any solvent produced by dissolving in a given volume of that solvent a number of grams of any undissociated substance equal to the molecular weight of the substance, we can then use the freezing-point lowering to determine the molecular weight of any substance in that solvent. If we dissolve a gram-molecular weight of an undissociated substance in a hundred grams of the solvent, the resulting freezing-point lowering is known as the freezing-point constant of the solvent. Knowing the freezing-point constant for any solvent, it is a comparatively simple matter to determine the molecular weight of any substance in that solvent.

We must weigh the solvent, also the amount of substance to be dissolved in the weighed amount of the solvent, and determine the lowering the freezing-point produced. Let the weight of the solvent be W, the weight of the dissolved substance w, the lowering of the freezing-point produced Δ, and the freezing-point constant C. The molecular weight of the substance M is calculated as follows: —

$$M = \frac{Cw}{\Delta W}.$$

The freezing-point constants of some of the more common solvents are given below : —

	Constant
Acetic acid	39.0
Benzene	50.0
Ethylene bromide	117.9
Formic acid	27.7
Nitro benzene	70.7
Water	18.6

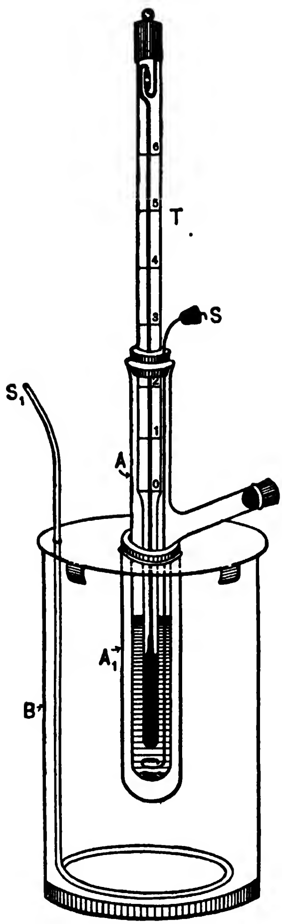


Fig. 17.

Apparatus devised by Beckmann. — The most convenient form of apparatus used for determining the value of Δ is that devised by Beckmann. It is shown in Fig. 17. The glass vessel A is to receive the solvent or solution whose freezing-point is to be determined. The substance can be introduced through the side-tube, but the latter can be readily dispensed with. The tube A passes through a cork into the wider glass tube A_1, and an air-space exists between the walls of the two tubes. The thermometer T is inserted into A, and fastened tightly in position by means of a cork. The liquid in A is stirred by means of a glass rod bent in a circle of sufficient diameter to allow the bulb of the thermometer to pass through. The stirrer is attached to a vertical rod S, and moved up and down by means of the hand. B is a battery jar, which contains the freezing-mixture. The substance used in the jar depends upon the freezing-point of the solvent with which we are dealing. If the solvent freezes appreciably above the freezing-point of water, it is only necessary to use water and ice. If we are working with water as the solvent, the freezing-mixture more commonly used is ice and salt. Care must be taken that not

too much salt is used, since, when the mixture is too cold, the results obtained are often not reliable.

The thermometer used by Beckmann requires special comment. It is constructed on a different plan from that of any other thermometer which has ever been employed. In the first place, the bulb is very large, and, consequently, the divisions on the scale correspond to a very small range in temperature. The largest scale divisions correspond to degrees. The total range of such a thermometer is usually about 6°. The next smaller divisions correspond to tenths of a degree, and the smallest divisions to hundredths of a degree. By means of a small lens it is possible to read the scale to thousandths of a degree.

The unique feature of the Beckmann thermometer is, however, the arrangement at the top. This is seen in Fig. 18.

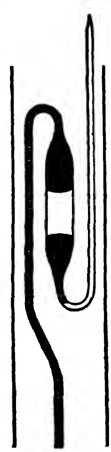


FIG. 18.

The capillary terminates in a reservoir or cistern, into which, by warming the bulb, mercury can be driven. The mercury in this reservoir can be thrown either to the top or bottom by holding the thermometer and tapping or thrusting it. By this means it is possible to increase or decrease the amount of mercury in the bulb of the thermometer, and to so adjust the amount that the top of the column will come to rest at any desired point on the scale, when the instrument is placed in the freezing solvent. The freezing-point of any solvent or solution can, then, be adjusted at any desired position on the scale, and the difference between the freezing-points of the solvent and solution determined. This differential thermometer of Beckmann has proved of incalculable service to physical chemistry, and has contributed more to our knowledge, in the field which we are now studying, than any invention or device which has ever been proposed.

Determination of the Molecular Weights of Dissolved Substances by the Boiling-point Method. — The determination of the molecular weights of dissolved substances by the boiling-point method is strictly analogous to the determinations by the freezing-point method. The boiling-point of a solvent is raised by the presence of dissolved substances, and the rise in boiling-point has been shown to be proportional to the lowering of the freezing-point. The rise in the boiling-point, like the lowering of the freezing-point, depends upon the ratio between the number of molecules of the dissolved substance and the number of molecules of the solvent. If we know the rise in the boiling-point of a solvent produced by a gram-molecular weight of

an undissociated substance in a hundred grams of the solvent, — the boiling-point constant of the solvent, — the determination of the molecular weight of any substance in that solvent is a comparatively simple matter.

If we represent the weight of the solvent used by W, the weight of the dissolved substance by w, the rise in the boiling-point by R, and the boiling-point constant by C, the molecular weight of the substance M is calculated as follows: —

$$M = \frac{Cw}{RW}.$$

The boiling-point constants of a few of the more common solvents are given below: —

	Constant		Constant
Acetone	17.1	Ether	21.6
Aniline	32.0	Ethyl alcohol	11.7
Benzene	26.1	Methyl alcohol	8.4
Carbon disulphide	23.5	Water	5.1
Chloroform	35.9		

Boiling-point Method of Beckmann. — The rise in the boiling-point of a solvent produced by a dissolved substance was determined for a long time by the method of Beckmann. The apparatus which he employed is shown in Fig. 19. The glass tube A contains the liquid whose boiling-point is to be determined. Into this liquid the thermometer dips as shown in the figure. In the bottom of the tube are placed glass beads, garnets, or platinum scraps, so as to secure a more uniform rate of boiling. A condenser is attached to the tube A, as shown in the figure. This tube is surrounded by a double-walled, glass jacket B, into which is introduced some of the same liquid whose boiling-point is to be determined in A. This is also provided with a return condenser. The liquid in B is boiled at the same time as the liquid in A, so that the innermost vessel is surrounded by a layer of liquid having the same boiling-point. The whole apparatus rests upon an asbestos box, and heat is supplied by a flame placed beneath. Beckmann has devised a number of modifications of this apparatus, but in the opinion of the writer none of them represents any marked improvement on the form just described.

The pure solvent is poured into the tube A, the filling-material (beads or garnets) introduced, and the thermometer inserted so that when the cork is forced into the top of tube A, the bulb of the thermometer is entirely covered by the liquid, but does not touch the glass beads. The mercury in the Beckmann thermometer is so adjusted that the top of the column comes to rest between the divisions 0° and 1° when the solvent boils. The vessel A is then carefully cleaned and dried, and after introducing the filling-material a weighed amount of the solvent is poured in. The thermometer is inserted and the condenser attached. Some of the pure solvent is poured into the vapor-jacket, and boiled simultaneously with that in the tube A. The position of the mercury is carefully noted on the thermometer, after the solvent has boiled about twenty minutes, and the barometer is also very carefully read. The flame is now removed and the solvent allowed to cool.

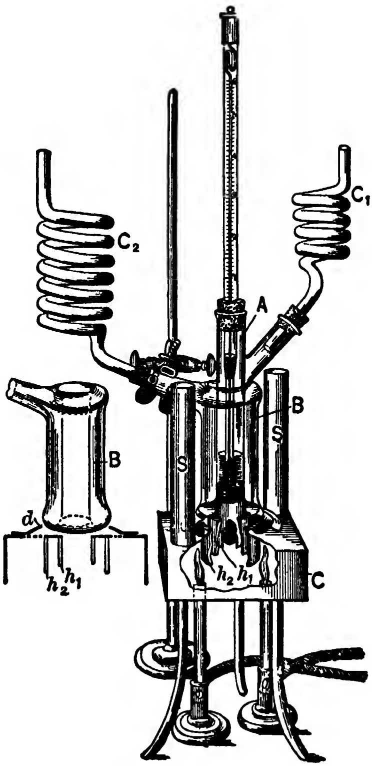


FIG. 19.

The substance whose molecular weight is to be determined is pressed into tablets, weighed, and introduced into the solvent. The boiling is renewed after all the substance has dissolved, and the temperature at which the solution boils carefully noted on the thermometer. The barometer is read again, and if any change has occurred the proper correction is introduced into the readings on the thermometer. Care must always be taken to tap the thermometer before making a reading. The difference between the boiling-point of the solvent and that of the solution is the rise in boiling-point produced by the dissolved substance.

Boiling-point Apparatus of Jones. — A number of attempts have been made to improve the boiling-point apparatus of Beckmann. The following form was devised and used by Jones: —

Into the glass tube *A* (Fig. 20) some glass beads or garnets are introduced. To the side-tube *A* the condenser is attached. Into the beads a cylinder of platinum *P*, is inserted by placing the finger upon the top of the cylinder and gently shaking the whole apparatus. The liquid whose boiling-point is to be determined is introduced into *A* until the bulb of the thermometer, placed as shown in the figure, is covered. The liquid must not come within a centimetre, or a centimetre and a half, of the top of the platinum cylinder. The tube *A* is surrounded by a thick jacket of asbestos *J*, and rests on an asbestos board in which a circular hole is cut, and over which a piece of wire gauze is laid. Heat is supplied by means of a very small flame *B*, placed beneath the apparatus and protected by a metallic screen as shown in the drawing.

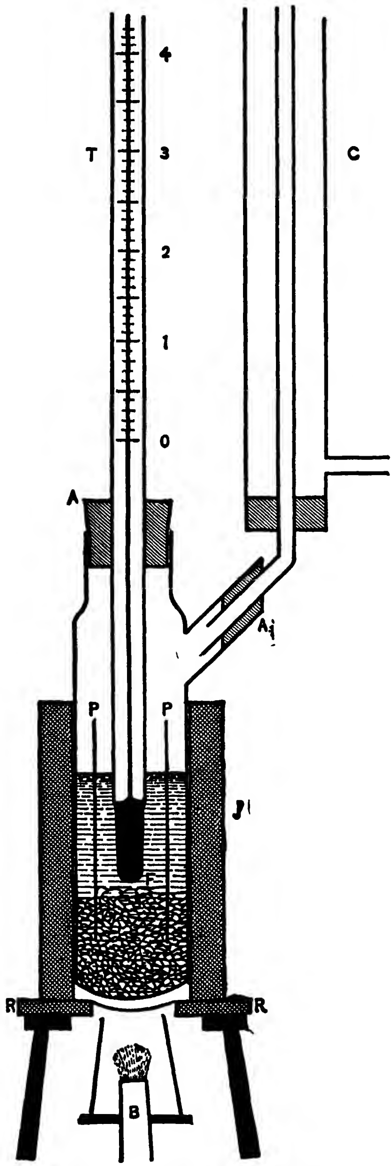


FIG. 20.

The essential difference between this apparatus and other forms is the platinum cylinder which is introduced into the boiling liquid. The object of this cylinder is twofold. It prevents the cooled, recondensed solvent from coming in contact with the thermometer before it is reheated to the boiling-point. It reduces the effect of radiation to a minimum. If the bulb of the thermometer is surrounded only by the boiling liquid, or even if a layer of asbestos is wrapped around the glass tube, heat will be radiated out from the hot bulb on to colder objects in the neighborhood.

The temperature of the bulb will always tend to be a little lower than that of the boiling liquid in which it is immersed. By surrounding the bulb with a piece of metal as nearly as possible at the same temperature as the bulb itself, the effect of radiation is reduced to a minimum.

The apparatus is exceedingly simple, and when applied to the determination of molecular weights of dissolved substances, was found to give good results in both low-boiling and high-boiling solvents. Another application of this method will be considered a little later.

CHAPTER VIII

OSMOTIC PRESSURE AND THE THEORY OF ELECTROLYTIC DISSOCIATION

Osmotic Pressure.—Having studied water as a solvent, we can turn to a class of phenomena which has come into great prominence in the last two years, and which directly and indirectly has thrown much light on chemical phenomena in general. If a solution of a substance in a solvent like water is placed in a vessel, and over this solution the pure solvent poured, we would find after a time that the substance is not all contained in that part of the solvent in which it was originally present, but a part of it has passed into the layer of the pure solvent which was poured upon the solution. This shows that there is some force analogous to a pressure, driving the dissolved substance from one region to another, from the more concentrated to the less concentrated solution. This pressure has been termed *osmotic pressure.*

Demonstration of Osmotic Pressure.—The existence of this pressure was early recognized. Abbé Nollet demonstrated its existence about the middle of the eighteenth century. A glass tube closed at the bottom with animal parchment was filled with ordinary alcohol, and the tube then immersed in water. Water could pass in through this parchment, but alcohol could not pass out. The contents of such a tube gradually increased in volume, showing to the eye the existence of osmotic pressure. During the first three-fourths of the last century osmotic pressure was demonstrated by filling an animal bladder with an aqueous solution of alcohol, and immersing the bladder in water. The water passed into the bladder and the alcohol could not pass out in any quantity. Hence, the bladder became distended and finally burst. It will be observed that in all of these experiments recourse was had to animal membranes. A discovery was subsequently made, which has entirely done away with the use of natural membranes in demonstrating osmotic pressure.

These membranes, which have the property of allowing the solvent to pass through them, and of preventing the dissolved substance from passing, are known as *semi-permeable.* It was M. Traube

who first prepared such semi-permeable membranes artificially. He found that certain precipitates, deposited in a suitable manner, have the property of allowing the solvent to pass through them, but hold back the dissolved substance. These precipitates include copper ferrocyanide, and a number of similar gelatinous substances. A method of demonstrating osmotic pressure, now that we can prepare artificial membranes, is the following: A glass tube about 2 cm. in diameter and 8 to 10 cm. long, is tightly closed at the bottom with vegetable parchment. This is soaked in water for some hours so as to drive out air-bubbles. The top of the glass tube is tightly closed with a rubber stopper, through which is passed a fine capillary tube about a metre in length. The end of the capillary should just pass through the cork, but must not protrude beyond its lower surface. The large glass tube is now immersed in a beaker, which is sufficiently deep to receive the entire tube. The tube is then firmly clamped in a vertical position. The beaker is filled with a three per cent solution of copper sulphate. The cork is then removed from the tube, and the latter completely filled with a three per cent solution of potassium ferrocyanide, to which enough potassium nitrate has been added to make from a one to a two per cent solution. The tube is then closed as tightly as possible with the cork through which the capillary passes, care being taken that no air-bubble remains beneath the cork. The apparatus is then set in a quiet place for some days. After a day or two, if the experiment is successful, the liquid will begin to rise in the capillary, and may reach a height of from 40 to 50 centimetres.

The experience of the writer has been that not all such experiments succeed. Indeed, the number which give a good demonstration of osmotic pressure is only about one-third of the total attempts which he has made. The frequent failure is doubtless due in part to the nature of the parchment used.

The method by which the semi-permeable membrane is formed in this case is almost self-evident. The copper sulphate from below passes into the parchment, and the potassium ferrocyanide from above also enters the parchment. The two meet right in the walls of the vegetable parchment. At the surface of contact they form the gelatinous precipitate of copper ferrocyanide in the walls of the parchment. The precipitate, deposited in this manner, has the property of semi-permeability — it allows the water to pass through and prevents the dissolved substances from passing. Since osmotic pressure always acts so that water passes from the more dilute to the more concentrated solution, the flow of water in this case is from the

copper sulphate on the outside to the potassium ferrocyanide and potassium nitrate on the inside. The liquid rises in the capillary due to the inflow of water through the semi-permeable membrane.

Morse's Method of Preparing Semi-permeable Membranes. — The demonstration of osmotic pressure has now become a very simple matter, due to a method devised in this laboratory by Morse, and developed by Morse, Horn, and Frazer.

"It occurred to the authors that if a solution of copper salt and one of potassium ferrocyanide are separated by a porous wall which is filled with water, and a current is passed from an electrode in the former to another electrode in the latter solution, the copper and the ferrocyanogen ions must meet in the interior of the wall and separate as copper ferrocyanide at all points of meeting, so that in the end there should be built up a continuous membrane well supported on either side by the material of the wall."

In order to remove the air contained in the walls of the cup they made use "of the strong *endosmose* which appears when a current is passed through a porous wall separating two portions of a dilute solution in which the two electrodes are immersed." A dilute, boiled solution of potassium sulphate was used for this purpose. "On passing the current between the electrodes in the direction of the one within the cup, the liquid in the cup rises with a rapidity which increases with the dilution of the solution, and with the intensity of the current. The water, in passing through the wall, appears to sweep out the air in an effective manner."

Having removed the air by means of endosmosis, the membrane was formed by filling the cup with a tenth-normal solution of potassium ferrocyanide, and immersing it in a tenth-normal solution of copper sulphate. One electrode of platinum was inserted into the cup, and the other of sheet copper completely surrounded the cup. The current was passed from the copper to the platinum electrode. As soon as the copper ions, moving with the current, came in contact with the $Fe(CN)_6$ ions moving against the current, a precipitate of copper ferrocyanide was formed in the wall of the cup. This gradually became more compact, as was shown by the fact that the resistance offered to the passage of the current rapidly increased.

The advantage of driving the ions into the wall by means of the current is that the membrane can be formed much more compactly than by simply allowing them to pass into the wall by diffusion. With such a cell it is possible to demonstrate osmotic pressure in a most satisfactory manner. When the cell is filled with a normal solution of cane sugar, closed with a cork through which a capillary

monometer passes, and immersed in pure water, the liquid will rise in the capillary at the rate of more than a foot an hour, and in two days a pressure of thirty feet of the sugar solution is easily secured. This so far surpasses all other demonstrations of osmotic pressure thus far devised, that they become insignificant by comparison. The demonstration of osmotic pressure on the lecture table by means of this method has become as simple a matter as many of the daily experiments in inorganic and organic chemistry.

This method promises much for the quantitative study of osmotic pressure. The ease with which the cells can be prepared, using *suitable* porous cups, and the great resistance offered by the membranes formed by the electrical method, bid fair to open up new possibilities in connection with the direct measurement of osmotic pressure. A number of measurements of the osmotic pressure of solutions of cane sugar and glucose, of concentration as great as normal, have already been made. *Pressures as high as 31.4 atmospheres have been measured.*

Several other semi-permeable membranes have already been prepared by Morse and his co-workers, using the electrolytic method. Of these perhaps the most important is ferric hydroxide, since this substance can be employed in investigating alkaline solutions.

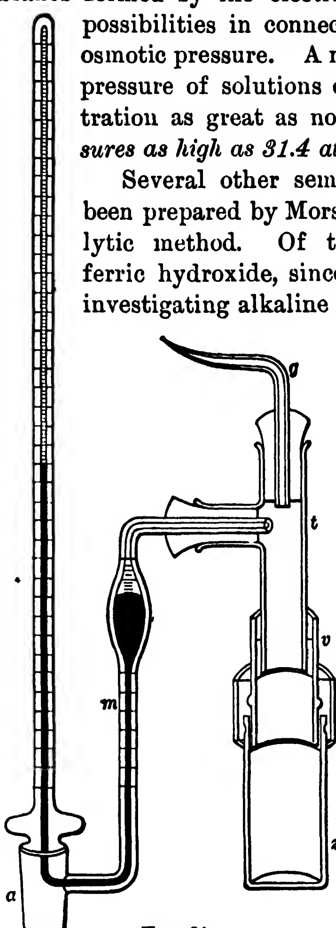


FIG. 21.

Measurement of Osmotic Pressure. — Certain measurements of osmotic pressure were made by W. Pfeffer twenty-seven years ago. He made use of the artificial membranes which had been discovered by Traube, and deposited them upon a support which was sufficiently resistant to enable them to withstand considerable pressure. Unglazed porcelain cells were injected with water and placed in a solution of copper sulphate. After a time they were filled with a solution of potassium ferrocyanide. The two substances enter the walls, the one from the inside, the other from the outside, and form a precipitated membrane of copper ferrocyanide. This appears as a fine, reddish-brown line in the walls of the porcelain.

The membrane once formed prevents either of the substances from passing through, and hence it appears as a fine line. In Fig. 21 is shown the apparatus used by Pfeffer. The manometer *m* is one-half natural size. The sketch is a longitudinal section of the apparatus. The cell *z* used by Pfeffer was only about 46 mm. high and 16 mm. internal diameter.

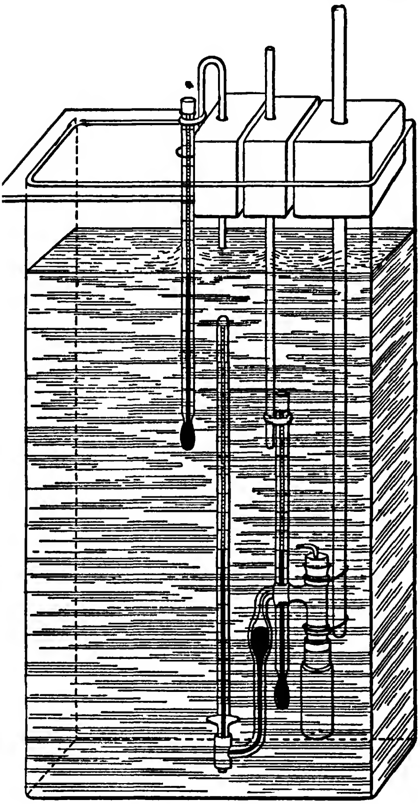


FIG. 22.

The measurements of osmotic pressure were made by means of these porcelain cells lined with the precipitate, which formed the semi-permeable membrane. After the manometer was attached to the cell, the latter was filled with the solution whose osmotic pressure was to be measured. The cell was then tightly closed and fastened to a glass rod as seen in Fig. 21.

The whole cell, including the manometer, was introduced into a bath as shown in Fig. 22. The bath was filled with pure water, and the osmotic pressure of the solution against pure water measured on the mercury manometer. Special precautions were taken to keep the temperature of the whole apparatus constant, since, as we shall see, there is a large temperature coefficient of osmotic pressure. The temperature of the experiment was accurately determined by means of carefully standardized thermometers.

RELATIONS BETWEEN OSMOTIC PRESSURE AND GAS-PRESSURE

Pfeffer carried out the measurements already referred to, and doubtless saw their physiological significance, but he did not point out any relations between osmotic pressure and gas-pressure. This,

like so many other brilliant discoveries, was reserved for Van't Hoff. In his epoch-making paper, he points out a number of surprisingly simple relations, and some of these will now be taken up.

Boyle's Law for Osmotic Pressure. — The law of Boyle for gases states that the pressure of a gas varies directly as the concentration of the gas. From Pfeffer's results, it has been shown that the osmotic pressure of a solution varies directly with the concentration. This relation for the osmotic pressure of solutions certainly suggests the relation for gases expressed by the law of Boyle.

Gay-Lussac's Law for Osmotic Pressure. — According to the law of Gay-Lussac the pressure of a gas increases with the temperature, at the rate of $\frac{1}{273}$ for every rise of 1° C. Pfeffer's results show that the osmotic pressure of a solution increases with rise in temperature, and the rate of increase is very nearly $\frac{1}{273}$ for every degree. Pfeffer did not make an extensive study of the temperature coefficient of osmotic pressure, but as far as his results go they led to the conclusion stated above.

If the law of Gay-Lussac applies to the osmotic pressure of solutions, then, solutions which are isosmotic, or have the same osmotic pressure at one temperature must remain isosmotic at other temperatures, since they would have the same temperature coefficient of osmotic pressure. This has been tested by the methods for determining relative osmotic pressures. Hamburger found that solutions of potassium nitrate, sodium chloride, and cane sugar, which were isosmotic at 0°, were also isosmotic at 34°.

There is, however, a still more striking experimental verification of the applicability of the law of Gay-Lussac to solutions. If a tube is filled with a gas and all parts of the tube kept at the same temperature, the concentration of the gas will be the same in every part of the tube. If, on the other hand, one portion of the tube is kept warmer than the others, the gas will so distribute itself throughout the tube that the pressure will remain the same in all parts of the tube. Since the pressure of gas increases with the temperature, each particle will exert a greater pressure in the warmer region, and, consequently, there will be fewer particles required in the warmer portion of the tube to exert the same pressure as exists in the colder portion. In a word, the gas would tend to become more concentrated in the colder portion, and more dilute in the warmer portion of the tube.[1]

[1] It should, of course, be remembered that the condition described for a gas is somewhat ideal. The gas particles, due to their rapid movement, would mix, but the principle which it is desired to illustrate holds good.

If the osmotic pressure of solutions obeys the laws of gas-pressure, a phenomenon similar to the above should be observed with solutions, and such is the fact. If the two parts of a perfectly homogeneous solution are kept at different temperatures for any considerable length of time, the solution becomes more concentrated in the region which is colder. This has come to be known from its discoverer as the *principle of Soret.* This principle is of the very greatest importance in testing the law of Gay-Lussac for osmotic pressure. If this law holds, then the colder portion of the solution should become more concentrated by $\frac{1}{273}$, for every difference of one degree in temperature. This could be easily tested by experiment. The experiments were carried out by Soret by placing the solutions in vertical tubes, in such a manner that the upper portions of the tubes were warmed to a constant temperature, and the lower portions cooled to a constant temperature. The earlier experiments of Soret gave a difference in concentration which was not quite as great as that calculated from the law of Gay-Lussac. His later experiments, in which the solutions were allowed to stand at constant temperatures for a longer time, gave differences which, while a little too low, yet accorded very nearly with the theory. A slight difference between calculated and experimental values creates no surprise when we consider that the solutions must stand for months at the constant temperatures in order that equilibrium may be reached, and some mixing of the parts due to agitation or jarring is, therefore, unavoidable. The agreement is, however, so close that it is now quite certain that the principle of Soret furnishes the best proof of the applicability of the law of Gay-Lussac to the osmotic pressure of solutions.

Avogadro's Law applied to the Osmotic Pressure of Solutions. — The applicability of the laws of Boyle and Gay-Lussac to the osmotic pressure of solutions, shows that this quantity is analogous to gas-pressure. It, however, leaves the question as to the relative magnitudes of the two pressures entirely unanswered. The one might be very large and the other very small, and still the two laws which we have just considered apply to both. We now come to the question, is there any close relation between the magnitudes of the two pressures exerted under comparable conditions?

The law of Avogadro, applied to gases, states that in equal volumes of all gases at the same temperature and pressure, there are the same number of ultimate parts. If the law of Avogadro applied to solutions, it would be stated thus: In equal volumes of solutions which, at the same temperature have the same osmotic pressure, there are contained the same number of dissolved particles. The

simplest way in which this law can be tested for solutions is to see what relation exists between the gas-pressure of a gas-particle and the osmotic pressure of a dissolved particle under the same conditions of temperature and concentration. Let us compare the gas-pressure of hydrogen gas and the osmotic pressure of cane sugar in water. Given a one per cent solution of cane sugar; such a solution would contain one gram of sugar in 100.6 cc. of water, and the osmotic pressure of such a solution can be calculated from Pfeffer's results. Hydrogen gas, having the same number of parts in a given volume, would have the following pressure: The molecular weight of cane sugar is 342, that of hydrogen 2. The hydrogen gas must, therefore, contain $\frac{2}{342}$ grams in 100.6 cm., which is the same as 0.0581 grams per litre. Hydrogen gas at 0°, and at a pressure of one atmosphere, weighs per litre 0.08995 gram; the above concentration of hydrogen gas will, therefore, exert a gas-pressure of $\frac{0.0541}{0.08995} = 0.646$ atmosphere at 0°.

It is now only necessary to compare the osmotic pressure exerted by the cane sugar with the gas-pressure, to see if any simple relations exist between the two. The following table of results is taken from the paper by Van't Hoff:—

Temperature	Osmotic Pressure of Cane Sugar	Gas-pressure of Hydrogen Gas
6°.8	0.664	0.665
13°.7	0.691	0.681
15°.5	0.684	0.686
36°.0	0.746	0.735

The remarkable fact is established by these results that *the osmotic pressure of a solution of cane sugar is exactly equal to the gas-pressure of a gas having the same number of parts in a given volume,* temperature being the same in both cases. Under the same conditions, then, a dissolved particle exerts the same osmotic pressure that a gas particle exerts gas-pressure.

Causes of Gas-pressure and of Osmotic Pressure.—That there should be an equality between these two pressures is very surprising, if we consider the great difference between the phenomena with which we are dealing. Gas-pressure is explained in terms of the kinetic theory of gases, as due to the particles of gas bombarding against the walls of the confining vessel. It should be stated that we do not know what is the cause of osmotic pressure. A great

number of explanations and theories have been offered to account for osmotic pressure, but in the opinion of the writer no one of them is at all satisfactory. Some have attempted to account for osmotic pressure by the attraction of water by the dissolved substance, but this is only a renaming of the phenomenon, and in no sense an explanation of it. Others have suggested that water passes through the semi-permeable membrane from the more dilute to the more concentrated solution, because of the screening action of the dissolved particles. These cannot pass through the membrane, and, therefore, screen it from the blows of the solvent. Since the greater screening influence is exerted on the side containing the larger number of dissolved particles, we have the flow of the solvent from the more dilute to the more concentrated solution. A careful analysis of this explanation shows that it is not sufficient. The screening influence of the dissolved particles would be just as great below as it is above, keeping the water which has passed through the membrane from rising, since the membrane is quite permeable to water. It is, therefore, fairest to say that we have at present no satisfactory theory to account for that phenomenon known as osmotic pressure.

Exceptions to the Applicability of the Gas Laws to Osmotic Pressure.—We have just seen that the three best known laws of gas-pressure apply to the osmotic pressure of solutions of substances like cane sugar. We might conclude from this that the laws of gas-pressure always apply to the osmotic pressure of solutions of all substances. Such is not the case. Van't Hoff pointed out that there are not only exceptions to this generalization, but a great many exceptions. Indeed, the substances which present exceptions are quite as numerous as those which conform to rule. The osmotic pressure of most salts, of all the strong acids, and all the strong bases, is much greater for all concentrations than would be expected from the osmotic pressure of solutions of substances like cane sugar for the same concentrations. The osmotic pressures of these three classes of substances are always greater than would be expected from the laws of gas-pressure applied to the osmotic pressure of solutions.

The general expression for the laws of Boyle and Gay-Lussac is, as we have seen,—

$$pv = RT.$$

This applies directly to the osmotic pressure of solutions of substances like cane sugar. But in order that it may apply to solutions of salts, acids, and bases, a coefficient must be introduced, which, for these substances, is always greater than unity. This coefficient

was called by Van't Hoff *i*, and it has come to be known as the Van't Hoff *i*.

The above expression when applied to acids, bases, and salts, becomes —

$$pv = iRT.$$

While these exceptions were clearly recognized by Van't Hoff, he was unable to explain them, or to offer any satisfactory theory to account for them.

In this case, as in so many others, the exceptions are as interesting and important as the cases which conform to rule. We shall see that these exceptions led to a theory which is one of the most important in modern chemical science.

ORIGIN OF THE THEORY OF ELECTROLYTIC DISSOCIATION

Work of Arrhenius. — Arrhenius was impressed by the generalizations reached by Van't Hoff connecting gas-pressure and osmotic pressure, and especially by the large number of exceptions to these generalizations. Referring to the equality of gas-pressure and osmotic pressure under the same conditions, Arrhenius found a difficulty in that the generalizations reached by Van't Hoff, connecting gas-pressure and osmotic pressure, held only for a large number of substances but by no means for all. The aqueous solutions of a great number of substances exerted a larger osmotic pressure than they should do if the generalization of Van't Hoff applied.

When a gas shows a deviation from the law of Avogadro we assume that it is dissociated, and verify the assumption experimentally. The same assumption may be made in the cases of substances which present exceptions to the laws of Van't Hoff.

Arrhenius then puts forward the assumption of the dissociation of certain substances dissolved in water to explain the exceptions to Van't Hoff's generalization. Osmotic pressure is, as we have seen, proportional to the concentration of the solution. This is the same as to say that osmotic pressure is proportional to the number of dissolved particles. If a substance exerts an abnormally great osmotic pressure, there must be more parts present in the solution than we would expect from the concentration. But acids, bases, and salts, represented by hydrochloric acid, potassium hydroxide, and potassium chloride, are the substances which show the abnormally great osmotic pressure. How is it possible to conceive of substances such as these breaking down into any larger number of parts than would correspond to their molecules?

This is the problem which must be solved, and Arrhenius has solved it, as we believe, satisfactorily. He went back to the theory proposed by Clausius to account for the facts which were known in connection with the phenomenon of electrolysis. It was found that an infinitely weak current will decompose water to which a little acid is added, liberating hydrogen at one pole and oxygen at the other. If the aqueous solution of the acid contained only molecules, in order that we might have electrolysis the current must be capable of decomposing the molecules. The fact is that a current far too weak to decompose a molecule of water will effect electrolysis. Therefore, some of the molecules present in the solution, either those of the water or of the acid, must be already broken down before the current is passed. Clausius did not claim that the molecules are broken down into their constituent atoms. Such a theory would be absurd. His theory was that the molecules are broken down into parts, which he called *ions*, and each ion is charged with electricity, either positively or negatively. An ion may be a charged atom or a charged group of atoms.

The theory that molecules are broken down into ions by a solvent like water was proposed, then, by Clausius in 1856.

A similar theory was advanced by the chemist Williamson in 1851, as the result of his work on the synthesis of ordinary ether from alcohol and sulphuric acid. The theory of Clausius differed from that of Williamson, in that the former assumed that there are only a few molecules broken down into ions, while Williamson thought that most of the molecules present are in a state of decomposition. It should be observed that both of these theories are purely qualitative suggestions. The one thought that only a few molecules in solution are broken down into ions, the other, that we have to do mainly with ions; but neither suggested any method by which we could determine the actual amount of the dissociation in any case.

The new feature which was introduced by Arrhenius was to point out a method for determining just what per cent of the molecules is broken down into ions. He thus converted a purely qualitative suggestion into a quantitative theory, which could be tested experimentally.

The Theory of Electrolytic Dissociation. — The theory of electrolytic dissociation, as we have it to-day, states that when acids, bases, and salts are dissolved in water, they break down or dissociate into ions. Examples of the three classes are the following: —

$$\text{[1] } HCl = \overset{+}{H}, \overset{-}{Cl}.$$
$$KOH = \overset{+}{K}, \overset{-}{OH}.$$
$$KCl = \overset{+}{K}, \overset{-}{Cl}.$$

Each compound dissociates into a positively charged part called a *cation*, and a negatively charged part, an *anion*. These ions may be charged atoms as the above cations, or groups of atoms as the anion OH. The cations are usually simple atoms charged with positive electricity. The cation of all acids is hydrogen, $\overset{+}{H}$; the nature of the anion varies with the nature of the acid. It may be chlorine, bromine, the NO_3 group, SO_4, etc. The anion of bases is the group $(\overset{-}{OH})$; the cation varies with the nature of the base. It may be potassium, barium, ammonium, etc. The anions and cations of salts both vary with the nature of the salt. They depend upon the nature of the acid and the base which have combined to form the salt.

Measurement of Electrolytic Dissociation. — Although electrolytes, which we remember include acids, bases, and salts, are dissociated by water into ions, it is not true that all electrolytes are completely dissociated under all conditions. Indeed, no electrolyte is completely dissociated by water, and still less by other solvents, unless the dilution of the solution is very great. The strongest acids, bases, and salts are completely dissociated only when the dilution is so great that a gram-molecular weight of the substance in question is dissolved in from five hundred to one thousand litres of water.

Electrolytes are dissociated, however, to a greater or less extent at all dilutions, and it is always a matter of interest and frequently a matter of importance to know the degree of the dissociation under the conditions in question.

Several methods are available for measuring the amount of dissociation of any electrolyte in a solvent like water. All electrolytes give *greater lowering of the freezing-point* and produce *greater rise in the boiling-point* of water than non-electrolytes. When we were discussing the determination of the freezing-point and boiling-point constants it was stated that non-electrolytes must be used. The reason is now apparent. Electrolytes being partly dissociated, contain a larger number of parts in solution than would correspond to their molecules. Since lowering of freezing-point and rise in boil-

[1] The comma between the two ions in this and all subsequent ionic equations means that the ions were combined as a molecule, or can combine and form a molecule.

ing-point are properties which depend only upon numbers, the larger the number of parts present, the greater the value of these quantities.

Knowing the lowering of the freezing-point and the rise of the boiling-point of water which would be produced if there were no dissociation, and knowing the values actually found, we calculate the amount of dissociation by simple proportion. If the depression of the freezing-point or rise of the boiling-point is twice as great as if there were no dissociation, the compound is completely dissociated, since each molecule yields two ions if the electrolyte is *binary* like those already considered. If the electrolyte breaks down into three ions, — is *ternary*, — these values are three times as large as if there is no dissociation.

If the values are one and one-half times as large as if there is no dissociation, it means that a binary electrolyte is dissociated fifty per cent, a ternary electrolyte twenty-five per cent, and so on. These examples will make the principle clear.

The Conductivity Method. — Another method is frequently used for measuring electrolytic dissociation. We have seen that solutions of electrolytes conduct the current, and indeed it is this property which characterizes a given substance as an electrolyte or a non-electrolyte. Solutions of electrolytes, however, conduct very differently even when the concentrations are the same. The amount of the conductivity has, however, been shown to depend upon the degree of the dissociation, and for any given electrolyte to be proportional to the number of ions present. In comparing conductivities, however, we must of course take into account the concentration. A *normal solution* in physical chemistry means one that contains a gram-molecular weight of the electrolyte in a litre of solution. Such a solution conducts better than a tenth-normal solution, but not ten times as well. To compare the conductivities of these two solutions we must divide that of the former by ten, or multiply that of the latter by ten. We adopt the second mode of procedure, and compare the conductivities of all solutions with those of the normal solution. Such are known as *molecular conductivities*, since they always refer to molecular quantities.

In the Kohlrausch method of measuring conductivity an alternating current is passed between platinum electrodes, through the solution whose conductivity it is desired to study. The resistance of the solution is balanced against a rheostat on a Wheatstone bridge, the point of equilibrium being determined by means of a telephone.

The apparatus used in the method of Kohlrausch is sketched in Fig. 23. W is a rheostat or set of resistance coils. The metre stick

AB is divided into millimetres, and over this is stretched a *manganine* wire (manganine being an alloy of German silver and manganese). *J* is a small induction coil which furnishes the alternating current. *R* is a glass cup which contains the solution whose resistance is to be measured. The electrodes are cut from thick sheet platinum, and a piece of platinum wire is welded into the centre of each plate. This wire is then sealed into a glass tube, which is filled

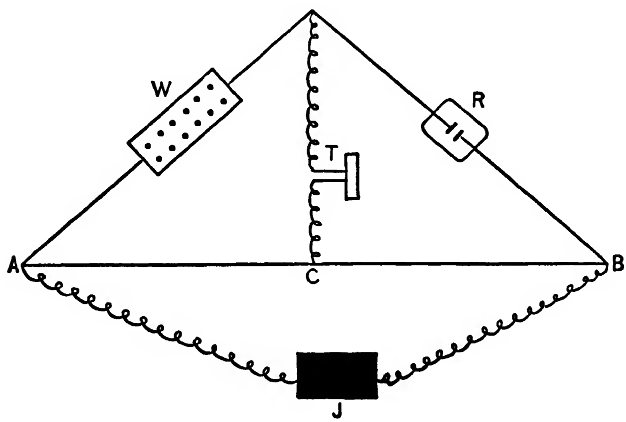


FIG. 23.

with mercury to make electrical contact with a copper wire introduced into the mercury. The telephone is connected between the rheostat and resistance vessel, and also with the bridge wire, by means of a slider. The point of equilibrium is ascertained by moving the slider along the wire until the sound of the coil is no longer audible in the telephone. Let this be a point *C*. Let us call the distance *AC*, a, *BC*, b, the resistance in the box r, and the resistance in the vessel r_1. From the principle of the Wheatstone bridge we would have—

$$rb = r_1 a;$$

$$r_1 = \frac{rb}{a}.$$

Since conductivity c is the reciprocal of the resistance r_1—

$$c = \frac{a}{rb}.$$

This expression does not take into account the concentration of the solution. In practice it is best to express concentrations in terms of gram-molecular weights of the electrolytes in a litre (gram-molec-

ular normal). As we have seen, the number of litres of the solution containing a gram-molecular weight of the electrolyte may be represented by ν, when the above expression becomes —

$$c = \frac{\nu a}{rb}.$$

By introducing ν into the above expression, we pass from specific to molecular conductivities, and we express the molecular conductivity by the letter μ. In order to indicate the concentration ν to which μ applies, we write for the molecular conductivity μ_ν —

$$\mu_\nu = \frac{\nu a}{rb}.$$

This expression takes into account all of the factors except the cell constant k, which depends upon the size of the electrodes which we are using, and their distance apart. Introducing the constant, we have —

$$\mu_\nu = k\frac{\nu a}{rb}.$$

Calculation of the Dissociation from Conductivity Measurements. — The molecular conductivity of an electrolyte increases with the dilution of the solution up to a certain point, where it acquires a maximum, constant value. This corresponds to the condition of complete dissociation, and is represented by the symbol μ_∞.

When there is no dissociation there is no conductivity. When there is partial dissociation the value of the molecular conductivity is between zero and μ_∞. These intermediate values of the molecular conductivity are represented as values of μ_ν; ν, representing the dilution of the solution or volume, is the number of litres of the solution which contains a gram-molecular weight of the electrolyte.

If we wish to know the percentage of dissociation α, at any dilution ν, it is only necessary to divide the value of μ_ν at that dilution by the value of μ_∞.

$$\alpha = \frac{\mu_\nu}{\mu_\infty}.$$

For details in applying the freezing-point, boiling-point, and conductivity methods to the measurement of electrolytic dissociation, some of the physical chemical manuals must be consulted.

CHAPTER IX

CHLORINE (At. Wt. = 35.45)

Chlorine an Element or a Compound. — Although chlorine does not occur in the free state, it was discovered as early as 1774 by the great Swedish chemist Scheele, who, however, did not recognize its elementary nature. The question of chlorine being an element or a compound is closely connected with an interesting chapter in the history of chemistry. It was thought at one period that oxygen is essential to acidity. In order that a compound should be an acid it must contain oxygen. Chlorine combines with hydrogen, forming one of the strongest acids known to man. The question arose where does the oxygen come from in the compound of chlorine with hydrogen, known at that time as muriatic acid? It was obvious that it could not come from the hydrogen, whose elementary nature was recognized at that time. It must, therefore, come from the chlorine. Chlorine was then regarded as an oxide of some element which was unknown, and which they could not isolate. However, it was termed murium, and chlorine was regarded as the *oxide of murium*. Hydrochloric acid, since it contained this oxide of murium, was known as "muriatic acid," a name which it bears even to-day. These views were held about 1785–1790.

The French chemist, Gay-Lussac, however, made it probable by his investigations that chlorine is an element, and this same conclusion was reached by the Englishman, Humphry Davy, in the early years of the nineteenth century.

During the last century a number of attempts were made to decompose chlorine into simpler substances, but all of these have failed; the evidence all pointing unmistakably to the elementary nature of chlorine.

Occurrence and Preparation of Chlorine. — Chlorine does not occur in the free condition in nature. This is due in part to its great chemical activity. If once set free it would quickly combine again with other substances. It occurs in combination with many other elements, such as magnesium, potassium, silver, lead, but especially in combination with the element sodium, as sodium chlo-

ride. The chlorides of all the above elements are readily soluble in water, except the chlorides of lead and silver. The soluble chlorides cannot exist on the surface of the earth, where they are subjected to the influence of water, but pass into solution and are swept down to the sea. This accounts for the large amounts of chlorine in sea-water, mainly in the form of potassium, magnesium, and sodium chlorides.

In certain protected localities, however, which are not readily accessible to water, as in the great salt beds of the earth, the chlorides may remain in solid form. As examples, take the great deposits at Stassfurt in Germany, Salzburg, and the like. The deposits were made by the evaporation of the seas which once covered these regions, and which contained the various salts in solution.

The more common minerals containing a large amount of chlorine are *carnallite*, *sylvine*, *rock salt*, and the like.

A number of methods have been devised for preparing chlorine, but most of these are now only of historical interest.

The process devised by *Deacon* consists in oxidizing hydrochloric acid by means of the oxygen of the air. Hydrochloric acid and air are passed through heated tubes containing balls of clay saturated with copper sulphate. Under these conditions the oxygen of the air unites with the hydrogen of the hydrochloric acid, forming water and liberating chlorine.

Another method for obtaining chlorine, based upon the oxidation of hydrochloric acid, is the following: —

When a compound rich in oxygen, like manganese dioxide, MnO_2, is heated with hydrochloric acid, the latter is oxidized to water and chlorine.

$$MnO_2 + 4\,HCl = MnCl_2 + 2\,H_2O + Cl_2.$$

A part of the chlorine combines with the manganese, forming manganese chloride, and is lost as far as free chlorine is concerned. A method (*Weldon's*) has been devised for obtaining this part of the chlorine by converting the chloride of manganese into an oxygen compound, but this is of little importance at present.

A very convenient method for obtaining chlorine in the laboratory consists in treating *bleaching-powder* with hydrochloric acid. The bleaching-powder is introduced into an ordinary Kipp's apparatus, and the acid allowed to come in contact with it. It will be remembered from the preparation of hydrogen that this apparatus works automatically. When no more gas is desired a stop-cock is closed, and the pressure of the gas liberated forces the acid away

from the bleaching-powder. The reaction which takes place here will be discussed under the element calcium.

All of these methods have practically given place to the *electrolytic*. Most of the chlorine is now prepared by the electrolysis of aqueous potassium or sodium chloride. When a solution of potassium chloride in water is electrolyzed, hydrogen separates at the cathode and chlorine at the anode. The potassium remains in solution around the cathode as potassium hydroxide. The following equation represents the reaction which takes place: —

$$2\,KCl + 2\,H_2O = 2\,KOH + H_2 + Cl_2.$$

In an analogous manner chlorine is prepared by the electrolysis of *carnallite*, a double chloride of potassium and magnesium having the composition $KMgCl_3$.

As already indicated, the electrolytic method has practically replaced all others for preparing chlorine on the large scale.

Chemical Properties of Chlorine. — The yellowish-green gas chlorine is, chemically, one of the most active substances known. It combines with nearly all the elements and with many compounds by simple contact, often with evolution of much heat and even light, and in some cases almost with explosive violence. The best method of collecting chlorine for experimental purposes is by displacement of air. Being heavier than air the chlorine gas is conducted to the bottom of the vessel containing air, and the latter is displaced upward by the heavier chlorine.

When copper foil is brought in contact with chlorine gas it combines with the chlorine, shown by the fact that it glows and forms chloride of copper.

$$2\,Cu + Cl_2 = 2\,CuCl,$$

or,

$$Cu + Cl_2 = CuCl_2.$$

When finely divided antimony is allowed to fall into a vessel containing chlorine gas, we have literally a rain of fire — each antimony particle becoming incandescent as it combines with the chlorine.

$$2\,Sb + 3\,Cl_2 = 2\,SbCl_3.$$

Phosphorus, boron, silicon, and other elements readily burn in chlorine, forming the corresponding chlorides. Other substances, like brass, burn in chlorine only when they have been heated to an elevated temperature.

Combustion in Chlorine. — We have here examples of combination taking place between substances and chlorine, which are analogous

to combustion in oxygen. In the former case, as in the latter, the combination takes place with evolution of light and heat, and the combustion in chlorine is even more energetic than in oxygen, in that it starts at ordinary temperatures. We have, then, *combustion in chlorine* just as truly as in oxygen. The term combustion, however, as ordinarily used, always refers to combination with oxygen, since we never know chlorine in the free condition unless it is specially prepared.

Action of Chlorine on Hydrogen. — Hydrogen unites with chlorine at ordinary temperatures if exposed to diffuse light, and with explosive violence if exposed to direct sunlight. A jet of hydrogen can, however, be burned in chlorine just as it can be burned in oxygen. When hydrogen was burned in oxygen, the two gases combined, forming water. When hydrogen is burned in chlorine, the two gases combine, forming the important compound hydrochloric acid, which we shall study a little later. Introduce a jet of burning hydrogen into a vessel filled with chlorine, and notice the pale green color of the flame, also the fumes of hydrochloric acid formed. A jet of chlorine also burns readily when plunged into a vessel filled with hydrogen gas.

Action of Chlorine on Water. — Chlorine is readily soluble in water, and the resulting solution is known as *chlorine water*. Chlorine water, if kept in the dark, is a stable substance, but if exposed to the light, a deep-seated change takes place. The chlorine acts chemically upon the water, combining with the hydrogen and liberating oxygen. The resulting solution contains the hydrochloric acid formed, while the oxygen gas is liberated. Such chemical reactions which are brought about by the action of light are known as *photochemical reactions*. We shall encounter a number of them as our subject develops. Since oxygen is liberated, chlorine is known as a *strong oxidizing agent*. Its oxidizing power renders chlorine one of the very best *bleaching agents* which is at our disposal. The oxygen which is set free when chlorine acts on moisture oxidizes organic coloring-matter, and leaves behind the colorless substance. This can be illustrated by bringing into the presence of chlorine gas some moist flowers or a moist piece of calico, when the color will disappear in a very short time.

Chlorine is also an excellent *disinfectant*, having an unusual power to destroy bacteria and other forms of life. This is due in part to its oxidizing action, and in part to direct combination of chlorine with the organic matter of such forms of life. All things considered, chlorine is one of the most powerful disinfectants known.

Action of Chlorine on Certain Organic Compounds. — Chlorine not only acts on elementary substances and simple compounds, but also

on complex organic substances. When brought in contact with the elements it combines with them in the proportions represented by the above equations. When brought in contact with organic substances which contain hydrogen, the chlorine first replaces the hydrogen, taking its place in the molecule, and then more chlorine combines with the replaced hydrogen, forming hydrochloric acid. Such a reaction, known as *substitution*, can be illustrated by bringing a piece of filter-paper saturated with oil of turpentine into a vessel filled with chlorine gas. A violent reaction takes place, resulting in the liberation of a large amount of finely divided carbon.

Oil of turpentine consists of carbon and hydrogen. The chlorine drives out the hydrogen in part at least, combining with it and forming hydrochloric acid, and leaves the carbon behind in the finely divided condition.

A better example of the substituting action of chlorine is its action on the compound benzene. Benzene also contains carbon and hydrogen, having the composition expressed by the formula C_6H_6. Chlorine displaces the hydrogen atoms, combining with them and also taking their place in the molecule:—

$$C_6H_6 + Cl_2 = C_6H_5Cl + HCl.$$

This process can be continued until all the hydrogen has been replaced by chlorine, the resulting compound being C_6Cl_6.

Chlorine Hydrate. — When chlorine gas is conducted into a mixture of water and ice, a crystalline compound separates, having a greenish color, and the composition is represented by the formula $Cl_2.8\,H_2O$ or $Cl_2.10\,H_2O$. At ordinary temperatures it decomposes into chlorine and water, while at somewhat elevated temperatures the decomposition is quite rapid, resulting in a copious evolution of chlorine gas.

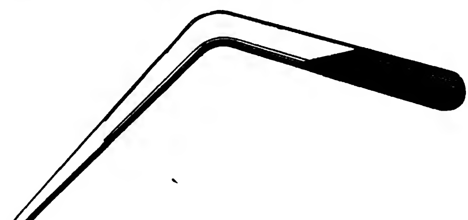


FIG. 24.

This compound is of special historical interest in connection with the liquefaction of chlorine, and also in connection with the liquefaction of gases in general. The earlier work on the liquefaction of gases was carried out almost exclusively by the great English physicist, Faraday. He succeeded in liquefying chlorine by means of chlorine hydrate. Some of this compound was placed in one end of a thick-walled glass tube, and the other end closed, as

shown in Fig. 24. The end of the tube containing the chlorine hydrate was gently warmed, while the other end was surrounded by a freezing-mixture of ice and salt. Under these conditions the chlorine was liberated, and produced a pressure in the tube which was sufficient to liquefy it. This is one of the classical experiments of Faraday on the liquefaction of gases.

PHYSICAL PROPERTIES OF CHLORINE

Certain Physical Properties of Chlorine. — The yellowish-green gas, chlorine, is about two and one-half times as heavy as the air, a litre weighing 3.22 grams. It has a most disagreeable odor, and an injurious effect when inhaled. It acts upon the mucous membrane of the nose and throat, and disintegrates these tissues if inhaled in sufficient quantity and for sufficient time. It is therefore necessary in working with chlorine to take every precaution to be protected from the gas. Such work should always be done under a good hood, with a strong draft to remove the gas as rapidly as it escapes into the air. Even when all ordinary precautions are taken, enough of the gas escapes into the atmosphere to be very unpleasant to the experimenter, and to produce uncomfortable results if inhaled for a sufficient time.

Chlorine does not obey the laws of Boyle or Gay-Lussac with the same exactness as oxygen and hydrogen. This is probably connected with the fact that chlorine at ordinary temperatures is below its critical temperature, and not far above its liquefaction temperature under atmospheric pressure. It is a general rule that gases near their point of liquefaction do not obey the gas-laws.

Liquefaction of Chlorine. — That chlorine can be liquefied with comparative readiness has been shown by Faraday's experiment, by means of which liquid chlorine was obtained from chlorine hydrate. At zero degrees a pressure of six atmospheres are required to liquefy chlorine, while under a pressure of one atmosphere it passes over into a liquid at $-33°.6$. This is the boiling-point of liquid chlorine. Its critical temperature, as shown by the experiment of Faraday, is above the temperature of a mixture of salt and ice, and, indeed, is quite high. It is 146°, and the pressure required to liquefy chlorine at this temperature is 94 atmospheres, this being the critical pressure of chlorine. Liquid chlorine has a specific gravity of 1.66 at $-80°$, but the coefficient of expansion is very large, and at higher temperatures the specific gravity is much less.

Liquid chlorine has a yellow color, showing little or none of the

green which is characteristic of the gas. It freezes at $-102°$, forming a greenish-yellow solid.

Comparative Inactivity of Dry Chlorine. — While moist chlorine is one of the most active substances chemically, dry chlorine is comparatively inactive. A lecture-table experiment, which is frequently shown, is to pass chlorine through a glass tube containing a piece of metallic sodium which is heated by means of a Bunsen burner. If the chlorine has been carefully dried, as is frequently done, the sodium will melt and remain with untarnished surface in contact with the chlorine gas. If, on the other hand, the water-vapor has not been removed from the chlorine, vigorous chemical action will take place, accompanied with intense heat and a bright light, and the compound sodium chloride will be formed.

The comparative inactivity of dry chlorine is further shown by the fact that liquid chlorine can be kept and transported in strong steel cylinders. Indeed, it can be obtained on the market in this form, and is the most convenient means of obtaining chlorine. The steel cylinders are provided with a stop-cock, so that when the gas is desired it is only necessary to open the stop-cock and obtain it.

We have already studied one reaction which would take place only when water was present — the union of hydrogen and oxygen. We shall meet later with a number of similar examples.

HYDROCHLORIC ACID

Hydrochloric Acid, HCl. — We have already examined a number of reactions in which hydrochloric acid was formed. We shall study more closely some of these, and other reactions in which hydrochloric acid is produced. We have seen that when hydrogen is burned in chlorine the product is hydrochloric acid. In order that this reaction should take place it is not necessary that an ignited jet of hydrogen should be introduced into the chlorine. We have seen that when the mixture is exposed to diffuse light a gradual combination takes place, and when exposed to direct sunlight the gases combine with explosive violence.

When hydrogen and chlorine gases are mixed in equal volumes, and an electric spark passed through the mixture, the gases combine with explosive violence. Such a mixture is known as *chlor-electrolytic gas*, or *chlorine detonating gas*, and is readily obtained by electrolizing a concentrated aqueous solution of hydrochloric acid.

Volume Relations in which Hydrogen and Chlorine Combine. — We have studied the relations by volume in which hydrogen and

oxygen combine, and the ratio between the volumes of the gases which enter into combination and the volume of the product formed. It will be remembered that one volume of oxygen combines with two volumes of hydrogen, and forms two volumes of water-vapor. The relations which obtain in the case of hydrogen and chlorine are even simpler. When one volume of hydrogen is mixed with one volume of chlorine and combination takes place, all of both gases are used up, and just two volumes of hydrochloric acid are formed. The law of the simple volume relations in which gases combine holds here even more strikingly than in the case of oxygen and hydrogen, there being no contraction in volume when the gases hydrogen and chlorine combine; and further, these gases combine in the simplest ratio by volume, viz. equality.

Preparation of Hydrochloric Acid. — Hydrochloric acid gas is prepared most conveniently on a large scale by a method entirely different from any of the above. When a salt of hydrochloric acid is treated with a non-volatile acid such as sulphuric, the hydrochloric acid gas is set free. The best known salt of hydrochloric acid is, as we have seen, sodium chloride. When this is treated with sulphuric acid, a reaction takes place in the sense of the following equation: —

$$2\,NaCl + H_2SO_4 = Na_2SO_4 + 2\,HCl.$$

The hydrochloric acid gas thus formed is conducted into water, which has the power of absorbing large quantities of it. This is the form in which it is used in the laboratory and in the arts. When it is desired to obtain the gas again from its concentrated solution in water, it is only necessary to add something to the solution which has greater attraction for water than the hydrochloric acid. Such a substance is ordinary sulphuric acid. When concentrated sulphuric acid is dropped slowly into concentrated, aqueous hydrochloric acid, the latter escapes from the solution as a continuous stream of gas.

Another method of preparing hydrochloric acid in quantity is by heating the chlorides of certain metals with water-vapor. The chloride of magnesium is frequently used, the reaction taking place in the sense of the following equation: —

$$MgCl_2 + H_2O = MgO + 2\,HCl.$$

Chemical Properties of Hydrochloric Acid. — Hydrochloric acid, as the name implies, is an acid, and since this is the first substance which we have thus far encountered with acid properties, a few words should be added in reference to acids in general. Hydrochloric acid has the composition represented by the formula HCl. Its molecule

therefore contains one atom of hydrogen and one of chlorine. The question arises to which constituent are the acid properties due? It may be due to either or to both. When we come to study other acids we shall learn that many substances are acids which do not contain any chlorine, and many compounds containing chlorine are not acids. Therefore chlorine is not essential to acidity. We shall also learn that all substances which are acid contain hydrogen, and no other element in common. Hydrogen is therefore essential to acidity.

There are, however, many compounds which contain hydrogen and which are not acids. The question which arises is how does the hydrogen in the latter class of compounds differ from the hydrogen in the former? The answer is furnished by the theory of electrolytic dissociation. When the compound hydrochloric acid is dissolved in water, its solution conducts the electric current. It is, therefore, an electrolyte, and its molecules are dissociated to a greater or less extent into ions. An aqueous solution of hydrochloric acid is, then, a solution of hydrogen and of chlorine ions.

As we shall have to deal frequently with ions, we adopt some method of distinguishing between atoms and ions. Since ions are charged atoms or groups of atoms, we shall use the positive sign over the symbol of an atom to mean that it is charged positively, or is a cation. The negative sign over an atom or group of atoms means that it is carrying a negative charge and is an anion. Hydrochloric acid is dissociated by water in the sense of the following equation: —

$$HCl = \overset{+}{H}, \overset{-}{Cl}.$$

When a solution of hydrochloric acid is brought in contact with a metal like zinc, the latter takes the positive charge from the hydrogen ion, becoming itself an ion and passing into solution, while the hydrogen ion having lost its electrical charge becomes an atom. We have seen, however, that an atom of hydrogen cannot exist by itself, two atoms combining and forming a molecule of hydrogen. The reaction between zinc and hydrochloric acid is represented by the following equation: —

$$Zn + \overset{+}{H}, \overset{-}{Cl} + \overset{+}{H}, \overset{-}{Cl} = \overset{++}{Zn}, \overset{-}{Cl}, \overset{-}{Cl} + H_2.$$

Hydrochloric acid acts upon metals in general in the sense of the above equation — the metal taking the charge from the hydrogen ion, becoming itself an ion, converting the hydrogen into the atomic condition. A few examples will make this clear.

$$K + \overset{+}{H}, \overset{-}{Cl} = \overset{+}{K}, \overset{-}{Cl} + H;$$

$$Ca + \overset{+}{H}, \overset{-}{Cl} + \overset{+}{H}, \overset{-}{Cl} = \overset{++}{Ca}, \overset{-}{Cl}, \overset{-}{Cl} + H_2;$$

$$Fe + \overset{+}{H}, \overset{-}{Cl} + \overset{+}{H}, \overset{-}{Cl} + \overset{+}{H}, \overset{-}{Cl} = \overset{+++}{Fe}, \overset{-}{Cl}, \overset{-}{Cl}, \overset{-}{Cl} + 3\,H.$$

Hydrochloric acid has also the power of acting chemically upon substances other than the metals. Indeed, the action of hydrochloric acid upon metals is not simply a chemical act, since it consists chiefly in the transfer of an electrical charge from the hydrogen ion of the acid to the metal.

Take a substance like calcium hydroxide — ordinary lime-water — having the composition $Ca(OH)_2$. When this is treated with hydrochloric acid a reaction takes place which we at present represent by the following equation, and will study it later in more detail: —

$$Ca(OH)_2 + \overset{+}{H}, \overset{-}{Cl} + \overset{+}{H}, \overset{-}{Cl} = \overset{++}{Ca}, \overset{-}{Cl}, \overset{-}{Cl} + 2\,H_2O.$$

Calcium hydroxide is a type of substances known as bases, with which we shall become familiar a little later. Hydrochloric acid acts in general upon bases.

Definition of an Acid. — Having studied hydrochloric acid as the type of a large class of chemical compounds known as acids, we are prepared to consider these a little more closely. The old conception was that acid properties depend for their existence upon the presence of oxygen. Indeed, the term *oxygen* means acid-former. This had to be abandoned after it was shown that many of our strongest acids contain no oxygen whatsoever.

As indicated above, all acids have certain properties in common. They all taste sour; they have the property of coloring certain vegetable dyes red. They have the power of dissolving certain metals in the sense of the above equations, and they all contain hydrogen which can give up its electrical charge to certain metals, itself escaping as hydrogen gas.

Hydrogen in this form is known as ionic hydrogen, and, as has been stated, wherever we have ionic hydrogen we have acid properties, and wherever we have acid properties we have ionic hydrogen. To say that a compound has acid properties means, then, that *when it is dissolved in water or some other dissociating solvent it yields hydrogen ions.*

This definition says that a compound is not an acid unless it is brought into the presence of a dissociating solvent. This is the same as to say that no pure, homogeneous substance is an acid. This seems on the face of it like going too far. Can we think of pure, dry hydrochloric acid, for example, as not having acid

properties? The definition goes still farther, and says that in order that a compound should have acid properties it must be dissolved in a dissociating solvent. If the definition is true, when a substance like hydrochloric acid gas is dissolved in a non-dissociating solvent, it should have no acid properties. To any one who is familiar with the strongly acid properties of hydrochloric acid when dissolved in water, this definition seems to lead to pretty serious consequences. What are the facts? Pure, dry, liquid hydrochloric acid has no acid properties. When pure, dry hydrochloric acid gas is dissolved in pure, dry, non-dissociating solvents like chloroform or benzene, the solutions have not the least trace of acid properties. A solution of dry hydrochloric acid gas in dry benzene will not even color blue litmus red. It should be added that such solutions do not conduct the electric current, showing that there are no ions, and, therefore, no hydrogen ions present. They have not the slightest power to dissolve metals, showing again that there are no hydrogen ions present to give up their charges to the metal atoms.

Such solutions would, however, taste sour, since as quickly as the molecules of the acid in the chloroform or benzene are brought in contact with the tongue, they are also in contact with moisture, and would be dissociated at once into hydrogen ions and chlorine ions. The hydrogen ions produce the characteristic sour taste of acids.

We shall learn that the above relations hold for all acids. No pure, dry, homogeneous substance is an acid. It becomes an acid only when dissociated by a solvent or some other means into hydrogen cations, and into anions whose nature depends upon the acid in question and varies with every acid.

Detection of Hydrochloric Acid.—There is one reaction which serves to detect hydrochloric acid under all ordinary conditions. Hydrochloric acid is, as we have seen, dissociated into hydrogen ions and chlorine ions. Any reaction which would detect hydrogen ions would not be a characteristic reaction of hydrochloric acid, since all acids when dissolved in water yield hydrogen ions.

To detect hydrochloric acid, then, we must make use of some reaction which is characteristic of the chlorine ion since all acids yield hydrogen ions. Such a reaction takes place whenever a silver ion is brought in contact with a chlorine ion.

$$\overset{+}{H},\ \overset{-}{Cl} + \overset{+}{Ag},\ \overset{-}{NO_3} = AgCl + \overset{+}{H},\ \overset{-}{NO_3}$$

expresses the reaction between hydrochloric acid and silver nitrate. The silver chloride formed is a white solid, readily soluble in ammonia. Since soluble chlorides in general yield in solution chlorine ions, this is a means of detecting also the presence of such chlorides.

Physical Properties of Hydrochloric Acid. — Hydrochloric acid is a colorless gas, with a sharp, pungent odor, and produces marked irritation of the mucous membrane of the nose and throat when inhaled even in small quantity. Its critical temperature is 52°, so that it can be readily liquefied. Its critical pressure is 82 atmospheres. At lower temperatures it can be liquefied at much lower pressures. At zero degrees it can be liquefied by a pressure of about thirty atmospheres.

Liquid hydrochloric acid is colorless, and as already indicated, is much less active chemically than the solution in water. Indeed, it is a comparatively inactive substance. When carefully freed from water it does not act on metals, and does not even color blue litmus red.

The liquid boils under atmospheric pressure at −80°.3, and solidifies at −112°.5. The gas shows unusual solubility in water, one volume of water at zero degrees dissolving about 503 volumes of the gas. The solubility diminishes as the temperature rises, which is in keeping with the general rule for the solubility of a gas in a liquid. The gas has such great attraction for water that if the breath is blown across the open mouth of a bottle of concentrated hydrochloric acid, the particles of water are condensed around the escaping hydrochloric acid, and a mist is produced which can be readily seen. The same effect is observed when the breath is blown into a stream of hydrochloric acid gas escaping from a generator.

Aqueous Solution of Hydrochloric Acid. — Hydrochloric acid gas dissolved in water is not a true solution of a gas in a liquid. That this is the case is shown in several ways. When hydrochloric acid gas is dissolved in water there is a marked evolution of heat, which does not take place when a gas is simply dissolved in a liquid. This would indicate that there is chemical union between the acid and water.

Further, when a solution of the gas in water is boiled even under diminished pressure, it is not possible to remove all the gas from the water, but a considerable portion remains dissolved in the water. When boiled under a pressure of 760 mm. gas escapes until the remaining liquid has a composition corresponding approximately to one molecule of hydrochloric acid and eight molecules of water. This mixture boils at a fairly constant temperature (110°), and does not change in composition, the distilled portion having the same composition as the undistilled liquid which remains behind. Further, if the aqueous solution of hydrochloric acid is more dilute than would correspond to this composition, water distils over until this composition is reached. All of these facts would indicate that this

particular mixture of hydrochloric acid and water is a definite chemical compound. It is well known that a chemical compound has a definite boiling-point, which is a characteristic constant of the substance.

There is one fact, however, which shows that this substance with a specific gravity of 1.102, and containing 20.3 per cent of hydrochloric acid is not a chemical compound. *Its composition changes* as we change the pressure under which it is boiled. If the pressure is greater than 760 mm., the distillate, or portion which distils over, contains more water in proportion to acid; while if the pressure is lower than the normal, the distillate is richer in acid than would correspond to one of acid to eight of water. This alone shows that the substance is not a chemical compound. Its constant composition when boiled under constant pressure is satisfactorily explained by physical chemistry, but it would lead us too far to discuss the subject in full in this connection. Suffice it to say that there are many such constant boiling mixtures known, none of which, however, are definite chemical compounds.

There is, however, a definite compound of hydrochloric acid and water which is well known. When hydrochloric acid gas is conducted into a concentrated aqueous solution of hydrochloric acid which has been cooled to $-22°$, well-defined crystals separate, having the composition $HCl.2H_2O$. These melt when heated to $-18°$, and decompose at higher temperatures.

When hydrochloric acid gas is dissolving in water, it is advisable to take one special precaution. The gas is so very soluble in water that if the tube through which the gas is escaping is plunged far beneath the surface of the water, the liquid is liable to rise rapidly in the tube and flow back into the generating flask.

An arrangement by means of which this can be avoided is the following: —

The generating flask is provided with an exit tube through which the gas escapes when the sulphuric acid acts on the sodium chloride. The end of this tube is provided with a funnel which dips just beneath the water in the receiver. If the water should tend to rise in the tube, due to the rapid absorption of the gas and the production of a partial vacuum in the tube, it will rise in the funnel until air can enter and restore the pressure to the normal. In this way the water is prevented from flowing back into the flask and breaking it while hot, or causing an explosion by contact with the sulphuric acid, which has become hot as the result of the chemical action.

This precaution is always taken when a very soluble gas is dissolved in a liquid.

COMPOUNDS OF CHLORINE WITH OXYGEN AND HYDROGEN

Compounds of Chlorine with Oxygen. — Although chlorine and oxygen cannot be made to combine directly, several compounds of these two elements have been made by indirect methods. These compounds are chlorine monoxide (Cl_2O), chlorine dioxide (ClO_2), and chlorine septoxide (Cl_2O_7). These compounds are all characterized by instability. They are prepared by methods with which we shall become familiar in our study of the compounds of chlorine with oxygen and hydrogen, and we shall therefore turn to this class of substances.

Compounds of Chlorine with Oxygen and Hydrogen. — Thus far we have studied compounds between only two elements. We might suspect, therefore, that only two chemical elements can combine with one another, forming a definite molecule, or at least that this is by far the most common form of chemical union. Such is by no means the case. We shall now study briefly a class of compounds between the three elements, chlorine, oxygen, and hydrogen, which, if not very common substances, have considerable chemical interest. These compounds are: —

Hypochlorous acid	$HClO$.
Chlorous acid	$HClO_2$.
Chloric acid	$HClO_3$.
Perchloric acid	$HClO_4$.

Hypochlorous Acid, HOCl. — Hypochlorous acid is formed in very small quantity when chlorine acts upon water, and in the sense of the following equation: —

$$H_2O + Cl_2 = HCl + HOCl.$$

The free hydrochloric acid formed also as the result of the reaction acts upon the hypochlorous acid and decomposes it. If there is some substance present to combine with the hydrochloric acid, such as freshly precipitated mercuric oxide, it is removed from the field of action and does not decompose the hypochlorous acid. The reaction between chlorine and water, then, takes place in the sense of the following equation: —

$$H_2O + 2\,Cl_2 + HgO = HgCl_2 + 2\,HClO.$$

Another method for preparing hypochlorous acid, which on the whole is the best, consists in preparing first the potassium or sodium salt of the acid. When chlorine is conducted into a cold, dilute

solution of potassium or sodium hydroxide, the reaction takes place in the sense of the following equations: —

$$2\,KOH + Cl_2 = KCl + KOCl + H_2O;$$
$$2\,NaOH + Cl_2 = NaCl + NaOCl + H_2O.$$

The salts of hypochlorous acid are termed hypochlorites. These salts, therefore, are potassium hypochlorite and sodium hypochlorite.

When either of these salts is treated with a cold, dilute solution of hydrochloric acid, the hypochlorous acid is set free: —

$$KOCl + HCl = KCl + HOCl.$$

The hypochlorous acid is then distilled off and collected.

Properties of Hypochlorous Acid. — Hypochlorous acid is a weak acid, and is an unstable compound. It readily gives up oxygen, passing over into hydrochloric acid: —

$$2\,HClO = 2\,HCl + O_2.$$

It is, therefore, a powerful oxidizing agent, and if brought in contact with substances which can take up oxygen, readily gives it up to them. Its value as a *bleaching agent* depends upon this fact.

Calcium Hypochlorite, $Ca(OCl)_2$. — The calcium salt of hypochlorous acid is used extensively as a bleaching agent, on account of the ease with which it gives up chlorine. When chlorine is passed into slaked lime, the following reaction apparently takes place: —

$$2\,Ca(OH)_2 + 2\,Cl_2 = CaCl_2 + Ca(OCl)_2 + 2\,H_2O.$$

This apparent mixture of calcium chloride and calcium hypochlorite is known as "bleaching-powder," and is largely used as a disinfectant.

Chlorine Monoxide, Cl_2O. — Hypochlorous acid is not known in the anhydrous condition. When an attempt is made to free it from water, it loses water itself and passes over into chlorine monoxide.

$$2\,HOCl = H_2O + Cl_2O.$$

The compound Cl_2O, since it is formed from hypochlorous acid by the removal of water, is also known as hypochlorous anhydride; the term *anhydride* of a substance being a generic term for a compound derived from another by loss of water. The most convenient method of preparing chlorine monoxide is by passing dry chlorine over dry, yellow, mercuric oxide.

$$HgO + 2\,Cl_2 = HgCl_2 + Cl_2O.$$

The chlorine monoxide, being a gas at ordinary temperatures, can be readily collected. It is readily converted into a dark-yellow liquid, which boils at $-19°$.

Gaseous chlorine monoxide is somewhat explosive, but the liquid is very explosive. By warming or jarring, it explodes easily, yielding chlorine and oxygen.

$$2\,Cl_2O = 2\,Cl_2 + O_2.$$

Chlorine monoxide dissolves readily in water, combining with it and forming hypochlorous acid.

$$Cl_2O + H_2O = 2\,HClO.$$

Chloric Acid, $HClO_3$. — The most convenient method of preparing chloric acid is first to prepare the potassium or barium salt, and from the salt to obtain the free acid. When chlorine gas is conducted into a hot, concentrated solution of potassium hydroxide, the following reaction takes place: —

$$6\,KOH + 3\,Cl_2 = 5\,KCl + KClO_3 + 3\,H_2O.$$

The solution contains, after the reaction is over, two salts, potassium chloride and potassium chlorate. These can, however, be readily separated by their different solubilities in water; potassium chloride being quite soluble, while potassium chlorate is very much less soluble.

From the solution potassium chlorate readily crystallizes, especially on evaporation, leaving behind in solution the potassium chloride. With potassium chlorate we have already become somewhat familiar when we were studying methods of preparing oxygen. It will be remembered that this compound gives off all of its oxygen when heated to an elevated temperature.

When potassium chlorate is treated with a dilute solution of sulphuric acid, the following reaction takes place: —

$$2\,KClO_3 + H_2SO_4 = K_2SO_4 + 2\,HClO_3.$$

Care must be taken not to treat potassium chlorate with concentrated sulphuric acid, since violent explosions almost always result from such a reaction.

The solution contains the chloric acid, but since the latter cannot be distilled without undergoing decomposition, this method does not yield pure chloric acid.

To obtain pure chloric acid a salt of this acid must be used which will form an insoluble precipitate with the sulphuric acid. The barium salt is the most convenient. When barium chlorate is treated with a dilute solution of sulphuric acid in equivalent quan-

tity, insoluble barium sulphate is precipitated, and pure chloric acid remains in solution.

$$Ba(ClO_3)_2 + H_2SO_4 = \underset{\text{}}{\overset{\text{(Insoluble)}}{BaSO_4}} + 2\,HClO_3.$$

The barium sulphate is then filtered off, or the clear, supernatant liquid decanted from the precipitate and concentrated in a vacuum or over sulphuric acid.

Chloric acid may also be prepared by the action of hydrochloric acid on silver chlorate, the silver chloride formed being insoluble.

Properties of Chloric Acid. — Chloric acid is a colorless liquid with very strongly acid properties and with great oxidizing power. It contains a large amount of oxygen, which it readily gives up. When chloric acid is warmed or exposed to the light, it passes over into perchloric acid, which we shall study a little later. When a piece of paper is saturated with a concentrated solution of chloric acid, it is oxidized so energetically that it bursts into flame.

Chlorates. — The chlorates, as the salts of chloric acid are called, are very energetic oxidizing agents. This is due in part to the large amount of oxygen which they contain, and in part to the ease with which they give it up. To illustrate the unusually strong oxidizing power of the chlorates and their decomposition products, perform the following experiment: Mix some finely powdered potassium chlorate with some finely powdered cane sugar, and place a small amount of the mixture on a stone slab under the hood. Add cautiously from a pipette a few drops of concentrated sulphuric acid. In a few moments the entire mass will burst into violent flame.

The Chlorine Ion and the Ion of Chlorates. — We have studied one of the characteristic properties of the chlorine ion, viz. its power to combine with the silver ion and form insoluble silver chloride. We would naturally ask whether the chlorine in potassium chlorate has this same power. When a solution of potassium chlorate is electrolyzed, the potassium ion moves to the cathode and the chloric ion $\overset{-}{ClO_3}$ to the anode. Potassium chlorate, therefore, dissociates as follows: —

$$KClO_3 = \overset{+}{K},\ \overset{-}{ClO_3}.$$

Chlorine in this case, instead of forming the anion, forms only a part of the anion. It is in combination with three oxygen atoms, and the chlorine and oxygen form the anion. If a solution of potassium chlorate is treated with a solution of silver nitrate, no precipitate is formed, showing that chlorine has very different properties when alone in the ionic state, than when combined with another element forming part of a complex ion.

Perchloric Acid, $HClO_4$. — When potassium chlorate is heated vigorously it gives off all of its oxygen, as we saw when we were studying methods for the preparation of oxygen. If, however, potassium chlorate is heated moderately, it gives off only a part of its oxygen. The decomposition of potassium chlorate by heat takes place, then, in two stages. In the first place the potassium chlorate melts and gives off oxygen. If the temperature is now kept constant, oxygen will cease to come off after a time and the melted substance will solidify. This solid mass is a mixture of potassium chloride and potassium perchlorate, and this reaction is in general formulated thus: —

$$2\,KClO_3 = KCl + KClO_4 + O_2.$$

It is, however, questionable whether this expresses the whole truth. The perchlorate, $KClO_4$, can be obtained from the mixture by dissolving out the potassium chloride by means of cold water in which potassium chlorate is very slightly soluble.

When potassium perchlorate is treated with sulphuric acid, perchloric acid is set free.

$$2\,KClO_4 + H_2SO_4 = K_2SO_4 + 2\,HClO_4.$$

When the solution is distilled under diminished pressure, perchloric acid passes over and is condensed. By fractional distillation under diminished pressure it can be obtained in pure condition.

Properties of Perchloric Acid. — Perchloric acid is more stable than any of the other oxygen and hydrogen compounds of chlorine. The pure acid is a very vigorous oxidizing agent, and explodes easily when brought in contact with substances which can be oxidized. The acid containing from thirty to forty per cent of water is, however, quite stable. Perchloric acid forms a definite, crystalline compound with water, having the composition $HClO_4.H_2O$.

Perchloric acid is a very strong acid, which is the same as to say that it is very much dissociated by water. It readily replaces hydrochloric acid from its salts, but this is partly due to the comparative insolubility of the perchlorates; it being a general law in chemistry that *when an insoluble compound can be formed it is formed.* If a fairly concentrated solution of potassium chloride is treated with perchloric acid, needles of potassium perchlorate are precipitated. Perchloric acid is one of the few substances which form difficultly soluble compounds with potassium and similar elements, and this reaction can therefore be used to detect the presence of perchloric acid.

Chlorine Septoxide, Cl_2O_7. — When perchloric acid is dried with the powerful dehydrating agent, phosphorus pentoxide (P_2O_5), water is removed and chlorine septoxide is formed.

$$2\,HClO_4 + P_2O_5 = P_2O_5.H_2O + Cl_2O_7.$$

Chlorine septoxide is a colorless oil, boiling without decomposition at 82°.

Chlorine Dioxide, ClO_2, and Chlorous Acid, $HClO_2$. — Chlorine combines with hydrogen and oxygen, forming an acid with more oxygen than hypochlorous, and with less oxygen than chloric acid. This acid was not taken up until we had studied chloric acid and the chlorates, since, in its preparation, a chlorate is used. When potassium chlorate is carefully heated with oxalic acid, at a temperature of about 70°, and the decomposition products passed through a freezing mixture of salt and ice, a reddish oil which is explosive condenses. This is chlorine dioxide, having the composition ClO_2. The same gas is formed when a chlorate is decomposed with sulphuric acid. The liquid boils at 10°, and passes over into a yellowish-red crystalline solid at −79°.

The gas and liquid are explosive. Indeed, it is this gas which explodes when potassium chlorate is treated with sulphuric acid. This gas dissolves in water without rendering the solution acid. When conducted into a solution of a strong alkali, such as potassium or sodium hydroxide, the following reaction takes place: —

$$2\,ClO_2 + 2\,KOH = H_2O + KClO_3 + KClO_2.$$

The new compound, $KClO_2$, which we have met with for the first time, is known as potassium chlorite, and is a salt of the acid, $HClO_2$, *chlorous acid*, which has thus far not been isolated.

Power of Chlorine to combine with Oxygen. — We have thus seen that there are a number of compounds of chlorine with oxygen, containing for one atom of chlorine very different amounts of oxygen. This shows that one element may combine with very different amounts of another element, and form definite chemical compounds. This raises the question, What is the true combining weight of chlorine? Are we to take the largest or the smallest amount of chlorine which enters into a molecule? We always take the smallest, and this is for us the atom. If we take the amount of chlorine which enters into the molecule, which we write Cl_2O, we find that it is just double the amount which combines with the element hydrogen to form hydrochloric acid. The amount of chlorine in a

molecule of hydrochloric acid is the smallest quantity of chlorine known; chlorine never combining with any element in a quantity which is smaller than that which enters into a molecule of this acid. This is for us the atom of chlorine, and all other quantities of chlorine are referred to this as the unit. The weight of this amount of chlorine is 35.45, on the basis of oxygen = 16.

Valence. — One atom of chlorine sometimes combines with a half atom of oxygen, *i.e.* two atoms of chlorine are required to combine with one atom of oxygen, as in the compound Cl_2O. In other cases, one atom of chlorine combines with two atoms of oxygen, as in ClO_2, while in the compound Cl_2O_7, one atom of chlorine combines with three and a half atoms of oxygen. The power of an atom to hold other atoms in combination is known as its valence. This is not to be taken as a definition, but simply as a description of the action of chemical valence.

We have already seen examples of chemical action taking place between ions, which are atoms or groups of atoms charged with electricity. There is abundant evidence furnished by physical chemistry, and some of this will be discussed later, that nearly all, if not all, chemical action is between ions or charged parts. The establishment of this fact has given us a definite physical basis for the conception of valence.

An ion is *univalent*, or can combine with one hydrogen atom, which is really the unit of valence, if it carries one electrical charge. An ion is *bivalent*, or can combine with two hydrogen atoms, which are equivalent under all ordinary conditions to one oxygen atom, if it carries two electrical charges; *trivalent*, if it carries three charges; *quadrivalent*, if it carries four charges; *quinquivalent*, if there are five charges upon it; *sexivalent*, if it carries six charges; *septivalent*, if there are seven charges connected with it; and *octivalent*, if it carries eight charges. There are no ions known which have a greater valence than eight, *i.e.* which have the power of combining with more than eight hydrogen atoms, or four oxygen atoms.

Faraday's Law the Basis of Chemical Valence. — It is obvious, from the above, that the law of Faraday lies at the basis of chemical valence. Faraday passed an electric current through a solution of an electrolyte, and observed that the amount of the electrolyte decomposed was proportional to the amount of current which had passed through the solution. On the basis of this experimentally established fact he enunciated the first part of his well-known law: —

The amount of chemical decomposition effected by the passage of the current, is proportional to the amount of electricity which flows through the conductor.

Since electricity can flow through a solution of an electrolyte only by being carried by the ions in the solution, the above part of Faraday's law shows that each ion of the same substance carries exactly the same amount of electrical energy.

Faraday determined also the amounts of different elements which are separated from their compounds, by passing the same current through solutions of these compounds. A generalization of very wide significance was reached, which is the second part of the law of Faraday: —

The amounts of the different elements which are separated by the same quantity of electricity bear the same relation to one another as the equivalents of these elements.

This is saying in other words that all univalent elements carry exactly the same quantity of electricity, all bivalent elements carry exactly twice this quantity, all trivalent elements three times the quantity, and so on. In a word, all univalent ions carry the same amount of electricity, and all polyvalent ions a simple, rational multiple of the amount carried by univalent ions — the multiple being the valence of the ion.

By referring all chemical valence to the law of Faraday, which is one of the few laws of nature to which no exception is known, we place what has hitherto been only a name for a large number of empirical facts, upon an exact physical basis.

We have studied thus far three elements which are more or less typical, — oxygen, hydrogen, and chlorine. There still remain more than seventy elements, and we might continue our study by taking these up more or less as suited our convenience. Such a treatment of chemical phenomena would, to say the least, not be scientific. This is especially true since certain deep-seated connections between various elements have been unmistakably established. Certain elements are very closely allied in all of their properties, while between others the relationship is more remote, and others still have very little in common. We shall now take a bird's-eye view of the field yet before us, and see what elements are related most closely to one another. These we shall naturally treat in close sequence in order that the resemblances and differences may be pointed out.

CHAPTER X

THE PERIODIC SYSTEM

Hypothesis of Prout. — Attempts were early made to discover relationships between the elements; also relationships between the chemical properties of the elements and certain of their physical properties, especially their atomic weights. One of the first of these was pointed out by Prout as early as 1815. He observed that the atomic weights of the elements as then determined were nearly all whole numbers when referred to hydrogen as unity. This suggested to him the hypothesis which bears his name, viz. that all the elements are simply condensations of hydrogen. The atoms of the different elements are composed of hydrogen atoms, the number being expressed by the atomic weight of the element. More accurate determinations of atomic weights have, however, shown that they are not all simple, whole numbers when referred to hydrogen as the unit, but in some cases differ markedly from whole numbers.

The hypothesis of Prout, while not true as stated by its author, undoubtedly contains the germ of a great chemical truth.

The Triads of Döbereiner. — The next to point out any important relation between the chemical properties of the elements and their atomic weights was Döbereiner, in 1825. He called attention to relations such as the following. If we add the atomic weight of calcium, 40.1, to that of barium, 137.4, and divide the sum, 177.5, by 2, the product is 88.7, which is very close to the atomic weight of strontium, 87.6. These three elements are obviously very closely related chemically.

Again, if we add the atomic weight of sulphur, 32.06, to the atomic weight of tellurium, 127.6, and divide the sum, 159.66, by 2, the product is 79.83, which is very close to the atomic weight of selenium, 79.2. The chemical relationship between these three elements is also very close, as we shall learn. Similar relationships between the atomic weights of other groups of three closely allied elements were pointed out by Döbereiner. These are known as the *Triads of Döbereiner.*

The Octaves of Newlands. — The question of relations between the atomic weights was taken up by Newlands. In his earlier

papers he pointed out connections between atomic weights and chemical properties, but it was not until 1864 that he announced any important discovery. In a brief note to the *Chemical News*, "On Relations among the Equivalents," he arranged the elements in the order of their equivalents, and stated that "it will be observed that elements having consecutive numbers frequently either belong to the same group or occupy similar positions in different groups. . . . The difference between the number of the lowest member of a group and that immediately above it is 7; in other words, the eighth element starting from a given one is a kind of repetition of the first, like the eighth note of an octave in music." In the following year Newlands announced his "Law of Octaves" in a very brief note: "If the elements are arranged in the order of their equivalents with a few slight transpositions, it will be observed that elements belonging to the same group usually appear on the same horizontal line. It will be seen that the members of analogous elements generally differ either by 7, or by some multiple of 7. In other words, members of the same group stand to each other in the same relation as the extremities of one or more octaves in music." The table given by Newlands brings out the relation to which he refers. It is of such historical interest that it should be given in this connection.

NEWLANDS'S TABLE

H	1	F	8	Cl	15	Co & Ni	22	Br	29	Pd	36	I	42	Pt & Ir	50
Li	2	Na	9	K	16	Cu	23	Rb	30	Ag	37	Cs	44	Tl	53
G	3	Mg	10	Ca	17	Zn	25	Sr	31	Cd	38	Ba & V	45	Pb	54
Bo	4	Al	11	Cr	19	Y	24	Ce & La	33	U	40	Ta	46	Th	56
C	5	Si	12	Ti	18	In	26	Zr	32	Sn	39	W	47	Hg	52
N	6	P	13	Mn	20	As	27	Di & Mo	34	Sb	41	Nb	48	Bi	55
O	7	S	14	Fe	21	Se	28	Ro & Ru	35	Te	43	Au	49	Os	51

A comparison of this table with the periodic system proper will show that it contains more than the germ of this important generalization.

The Periodic System of Mendeléeff and Lothar Meyer. — The periodic system of the elements, as we now have it, was undoubtedly discovered independently, and very nearly simultaneously, by the Russian, Mendeléeff, and the German, Lothar Meyer. The latter published in 1864 a table containing most of the then known elements, arranged in the order of their atomic weights. In this arrangement elements which are closely allied in their chemical

properties appear in the same columns, but the system is so incomplete that it is scarcely an advance on that of Newlands.

The first to point out the most important features in the arrangement of the elements according to their atomic weights was undoubtedly Mendeléeff. In 1869 he arranged the elements in a table in the order of their atomic weights, and showed clearly that there is a periodic recurrence of properties as the atomic weights increase. This will be seen best in the following table:—

MENDELÉEFF'S ORIGINAL TABLE

Series	Group I — R_2O	Group II — RO	Group III — R_2O_3	Group IV RH_4 RO_2	Group V RH_3 R_2O_5	Group VI RH_2 RO_3	Group VII RH R_2O_7	Group VIII — RO_4
1	H=1							
2	Li=7	Be=9.4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27.3	Si=28	P=31	S=32	Cl=35.5	
4	K=39	Ca=40	— =44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63
5	(Cu=63)	Zn=65	— =68	— =72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	Y=88	Zr=90	Nb=94	Mo=96	— =100	Ru=104, Rh=104, Pd=106, Ag=108
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	I=127	
8	Cs=133	Ba=137	Di=138	Ce=140	—	—	—	— —
9	(—)	—	—	—	—	—	—	— —
10	—	—	Er=178	La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	— —
12	—	—	—	Th=231	—	U=240	—	— —

This table contains all the elements known at that time, and the blank spaces indicate that the elements which would naturally fall into these places were unknown. The general plan of the Mendeléeff table is simple. All the elements are arranged in succession in the order of their increasing atomic weights. If we start with the element with the smallest atomic weight next to hydrogen, *i.e.* lithium, and arrange the succeeding elements in the order of their atomic weights up to fluorine, we find that the next element, sodium, has properties quite similar to those of lithium. If we place sodium in the same vertical column with lithium, and then arrange the next elements in the order of their atomic weights, we find that magne-

sium falls in the same column with beryllium or glucinum, aluminium with boron, silicon with carbon, phosphorus with nitrogen, sulphur with oxygen, and chlorine with fluorine. This is, of course, a remarkable relation, since in every case those elements which fall in the same vertical column resemble each other very closely. The first seven elements, starting (not with hydrogen, since it does not fit into this scheme) with lithium, and ending with fluorine, agree very closely in properties with the second set of seven elements arranged as in the above table. We come now to the first member of the next series of seven elements, — potassium; it falls right into the group with lithium and sodium, calcium with glucinum and magnesium, titanium with carbon and silicon, vanadium with nitrogen and phosphorus, chromium with oxygen and sulphur, and manganese with fluorine and chlorine. Here again striking analogies appear between the different members in the same groups. The blank space between calcium and titanium contained no known element when this table was prepared. The element has since been discovered, and has peculiar interest in connection with this whole system; to this reference will again be made. After we leave manganese we encounter one of the weakest points of the Periodic Law. The next elements in order of atomic weights are iron, cobalt, and nickel; but it is obvious that neither of these can be placed in the same group with the alkali metals. They must, therefore, be set aside and left out of the system. Then we come to copper, which is very questionably placed with the members of group I. Then irregularities appear again. At the end of the sixth series we find three or four more elements which do not fit into the scheme, but after leaving these, regularities again begin to manifest themselves.

A more detailed account of the relations between properties and atomic weights will be taken up a little later. The above suffices to show the general relation, and also the periodic recurrence of properties with increase in the atomic weights.

The same general relations as those pointed out by Mendeléeff were undoubtedly discovered independently by Lothar Meyer, and published the following year (1870). His table is almost exactly the same as that of Mendeléeff, and he recognized clearly the periodic recurrence of properties. To quote his own words, "We see from the table that the properties of the elements are, for the most part, *periodic* functions of the atomic weights."

Meyer has since changed the form of this table, arranging it as a spiral. "If we regard this table as wrapped around an upright cylinder so that the right and left sides touch; therefore, nickel next

to copper, palladium to silver, and platinum to gold, we obtain, as is easily seen, a continuous series of all the elements in the order of their atomic weights, arranged in the form of a spiral. The elements which, in this arrangement, fall into the same vertical column, form a natural family, the members of which, however, bear a very unequal resemblance to one another." This spiral arrangement of the elements is shown in the following table: —

Meyer's Table (using the present atomic weights)

I	II	III	IV	V	VI	VII	VIII		
Li 7.03	Be 9.1	B 11.0	C 12.0	N 14.04	O 16.0	F 19.1			
Na 23.05	Mg 24.36	Al 27.1	Si 28.4	P 31.0	S 32.06	Cl 35.45			
K 39.15	Ca 40.1	Sc 44.1	Ti 48.1	V 51.2	Cr 52.1	Mn 55.0	Fe 55.9	Co 59.0	Ni 58.7
Cu 63.6	Zn 65.4	Ga 70.0	Ge 72.5	As 75.0	Se 79.2	Br 79.96			
Rb 85.5	Sr 87.6	Y 89.0	Zr 90.6	Nb 94	Mo 96.0		Ru 101.7	Rh 103.0	Pd 106.5
Ag 107.93	Cd 112.4	In 115.0	Sn 119.0	Sb 120.2	Te 127.6	I 126.97			
Cs 132.9	Ba 137.4	La 138.9	Ce 140.25						
		Yb 173.0		Ta 183	W 184.0		Os 191.	Ir 193.0	Pt 194.8
Au 197.2	Hg 200.0	Tl 204.1	Pb 206.9	Bi 208.5					
			Th 232.5		U 238.5				

This table brings out more clearly than that of Mendeléeff the idea of a continuous arrangement of all the elements in the order of their atomic weights. And it is equally successful in showing the periodic nature of the properties of the elements. The blank spaces are for unknown elements. Meyer calculated the probable atomic weights of these elements, but these values being for the most part unverified, are omitted.

Modification of Mendeléeff's Table

Series	Group 0	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII
	–	–	–	–	RH_4	RH_3	RH_2	RH	
	R	R_2O	RO	R_2O_3	RO_2	R_2O_5	RO_3	R_2O_7	RO_4
1		H = 1.008							
2	He = 4.0	Li = 7.03	Be = 9.1	B = 11.0	C = 12.0	N = 14 04	O = 16.0	F = 19.0	
3	Ne = 20.0	Na = 23.05	Mg = 24 36	Al = 27 1	Si = 28 4	P = 31 0	S = 32.06	Cl = 35.45	
4	A = 39.9	K = 39.15	Ca = 40.1	Sc = 44.1	Ti = 48.1	V = 51.2	Cr = 52.1	Mn = 55.0	Fe = 55 9, Ni = 58.7 Co = 59.0, Cu = 63.6
5		Cu = 63.6	Zn = 65.4	Ga = 70 0	Ge = 72 5	As = 75.0	Se = 79 2	Br = 79.96	
6	Kr = 81.8	Rb = 85.5	Sr = 87.6	Y = 89.0	Zr = 90.6	Nb = 94 0	Mo = 96 0		Ru = 101 7, Rh = 103.0 Pd = 106.5, Ag = 107.93
7		Ag = 107.93	Cd = 112.4	In = 115.0	Sn = 119 0	Sb = 120.2	Te = 127.6	I = 126.97	
8	Xe = 128.0	Cs = 132. 9	Ba = 137.4	La = 138.9	Ce – Yb * 140.25 to 173.0	Ta = 183.0	W = 184.0		Os = 191 0, Ir = 193.0 Pt = 194.8, Au = 197.2
9		Au = 197 2	Hg = 200 0	Tl = 204 1	Pb = 206.9	Bi = 208.5			
10					Th = 232.5	U = 238.5			

* This includes the following elements: Praseodymium = 140.5, Neodymium = 143 6, Samarium = 150 3, Terbium = 160.0, Erbium = 166.0, Ytterbium = 173 0: also a number of more or less doubtful elements with supposed atomic weights between 140 and 173.

One of the newest forms of the Periodic System, and in some respects the best, is the following, which was recently proposed by Brauner. This includes in group 0 the rare elements discovered in the atmosphere by Ramsay; however, this addition to the system was made some time ago by Ramsay himself. The distinctive features of this arrangement are; the grouping of a number of the closely related, rare elements in group IV, series 8. These elements have atomic weights ranging from 140 to 173. The ninth series in the Mendeléeff table, which contains no elements, is entirely abandoned; the tenth series is made an extension of the eighth, while the eleventh and twelfth series in the Mendeléeff table are made the ninth and tenth series in the new table.

This system has marked advantages over the earlier forms. It includes all the known elements, and what is more important, it omits the ninth series in the Mendeléeff table, which never had any real existence, since not a member of this series has ever been discovered. It also simplifies the system by reducing the number of series from twelve to ten; and what is perhaps most important, it brings together those elements which differ from one another in properties less than any other known elements.

CHEMICAL PROPERTIES AND ATOMIC WEIGHTS
COMBINING POWER

If we start with lithium in Mendeléeff's table and proceed to the right along the second series, this striking fact is observed; the elements increase in their power to combine with oxygen regularly from left to right. Take first the power of the elements to combine with oxygen. Lithium forms the compound Li_2O, beryllium BeO, aluminium Al_2O_3, carbon CO_2, nitrogen N_2O_5; oxygen and fluorine may be disregarded for the moment. Take the third series. Sodium forms the compound NaO, which is a superoxide, magnesium MgO, aluminium Al_2O_3, silicon SiO_2, phosphorus P_2O_5, sulphur SO_3, and chlorine Cl_2O_7. The fourth and fifth series show the same regularities, and similar relations are observed throughout the table. The best example of an element octivalent towards oxygen is osmium, which forms the compound OsO_4. We have, then, NaO, MgO, Al_2O_3, SiO_2, P_2O_5, SO_3, Cl_2O_7, OsO_4.

We may say in general that the power of the elements to combine with oxygen is smallest in group I, and increases regularly by unity in each succeeding group; reaching a maximum in group VIII, where, at least in the case of osmium, it is eight.

Results of a similar character are obtained if we study the power of the elements to combine with chlorine. Sodium combines with one chlorine atom, magnesium with two, aluminium with three, silicon with four, phosphorus with five. Sulphur does not combine directly with six chlorine atoms, but combines with both oxygen and chlorine, forming the compound SO_2Cl_2, in which the sulphur has a valence of four towards the oxygen, and of two towards the chlorine, or of six in all. But there is a member of group VI which combines directly with six chlorine atoms. This is tungsten, in the tenth series. We would express the combining power of the elements towards chlorine as follows: —

$$\begin{array}{cccccc} NaCl, & MgCl_2, & AlCl_3, & SiCl_4, & PCl_5, & SO_2Cl_2. \\ & & & & & (WCl_6) \end{array}$$

Exactly the same regularity which was observed in the case of oxygen exists here. The elements in group I have the smallest power to combine with chlorine, and this increases by unity from group to group as we pass from left to right; reaching a maximum of six in the sixth group. We know of no element that has the power of combining directly with more than six atoms of chlorine.

When we examine the power of the elements to combine with hydrogen, a regularity is observed, but of a different kind from those already considered. The elements in groups I, II, and III in general do not combine directly with hydrogen to form stable compounds, although hydrides of some of these elements are known. When we come to group IV, we find in carbon a remarkable power to combine with hydrogen. The highest valence of the elements towards hydrogen is manifested in this group, where one atom of the element combines directly with four atoms of hydrogen. As we pass to the right, the power of the elements to combine with hydrogen decreases, and decreases regularly. Nitrogen combines with three atoms of hydrogen, oxygen with two, and fluorine with one. Starting with group IV, we have: —

$$CH_4, \quad NH_3, \quad OH_2, \quad FH.$$

The valence towards hydrogen manifests itself to a maximum degree in group IV, and diminishes regularly as the valence towards oxygen increases.

The relations pointed out between the combining power of the elements are general, extending throughout the entire table of the elements. It should, however, be stated here that there are many breaks in the system, irregularities appearing on every hand. Some of these defects will be pointed out in a later paragraph.

Relations within the Groups

In the table of Mendeléeff the members of the even series are placed above one another, and, similarly, the members of the odd series. Each group is thus divided into two columns, whose meaning at first sight is not so apparent. If the members of these two columns in any group be compared, it will be found that those elements which fall in the same column are more closely allied in their general properties than the elements in different columns in the same group. Thus, lithium, potassium, rubidium, and cæsium resemble each other chemically more closely than they resemble sodium, copper, silver, and gold. This is more strikingly shown by the second group, where glucinum, calcium, strontium, and barium fall in one column, and magnesium, zinc, cadmium, and mercury in the other. The chemical relation between the individuals in a given column is very close in this group, while it is not so striking between the members of the different columns. Thus, calcium is much more closely related to strontium and barium than it is to zinc or mercury; and, similarly, cadmium is much more closely allied to zinc and mercury than it is to the calcium group.

Passing to the last group, chlorine, bromine, and iodine fall in the same column, and are very similar in their chemical behavior, while their relation to manganese is at first sight not very close. These facts, while purely empirical, are of profound interest, and give to the Periodic Law a deep significance. It is certainly true that the members of even series are more closely related to one another than they are to members of odd series, and the same obtains for the relations between the odd series. We seem to have here not only a Periodic System of the elements, but one such system within another.

Basic and Acid Properties

At least one other relation between the chemical properties of the elements and their atomic weights must be pointed out. In any given series the element with the lowest atomic weight has the smallest power to combine with oxygen, as has already been stated. It has also the strongest basic character. Thus, lithium is more basic than glucinum, which, in turn, is far more basic than boron. Sodium is more basic than magnesium, while aluminium begins to show acid properties in its hydroxide. Potassium is far more basic than calcium, rubidium than strontium, cæsium than barium. The difference between copper and zinc, and silver and cadmium, is not so striking. As we find the most basic elements in the first

group, we would expect to find the most acid in the last, and such is the case. Through the middle groups we find elements which show, now more, now less basic or acid properties, depending upon conditions; but in the last column of the last well-defined group we have elements which manifest only acid-forming properties. The hydrogen and hydroxyl compounds of the halogens are always acids, and always react as such with all other substances. These facts are very surprising. As we pass upward in the table of atomic weights, say from oxygen, the first element we encounter is fluorine, with very pronounced acid-forming properties. The element with the next higher atomic weight is sodium, which is one of the strongest base-forming elements. Similarly, next to sulphur comes chlorine, which has much stronger acid-forming properties than sulphur, but next to chlorine comes potassium, which is one of the most strongly basic elements. In the same way bromine is followed by rubidium, and iodine by cæsium, where the contrast in properties is quite as great as in the cases referred to above.

Many other relations between chemical properties and atomic weights have been pointed out, but those already considered are among the most important.

Physical Properties and Atomic Weights. — The relations between many of the physical properties of the elements and their atomic weights are striking. A number of these have been pointed out by Lothar Meyer.

Atomic Volumes. — The atomic volume of an element is the atomic weight divided by the specific gravity or density of the element in the solid form. In this connection the atomic weight of hydrogen is taken as the unit, and the specific gravity of water as the unit of density. Take the first element in the Periodic System which exists normally in the solid state, — lithium. Its atomic weight is 7, its density 0.059. The atomic volume of lithium $= \frac{7}{0.059} = 11.9$.

Meyer plotted the curve showing the change in the atomic volume with increase in atomic weight, and found that it had remarkable properties. The curve is shown in Fig. 25. The abscissas are atomic weights, and the ordinates atomic volumes.

In some cases the specific gravity of the element in the solid form could not be determined; as with hydrogen, oxygen, nitrogen, fluorine, etc. In the places corresponding to these elements the curve is a dotted line.

We see at once from the curve that the atomic volume is a periodic function of the atomic weight. As the atomic weight increases,

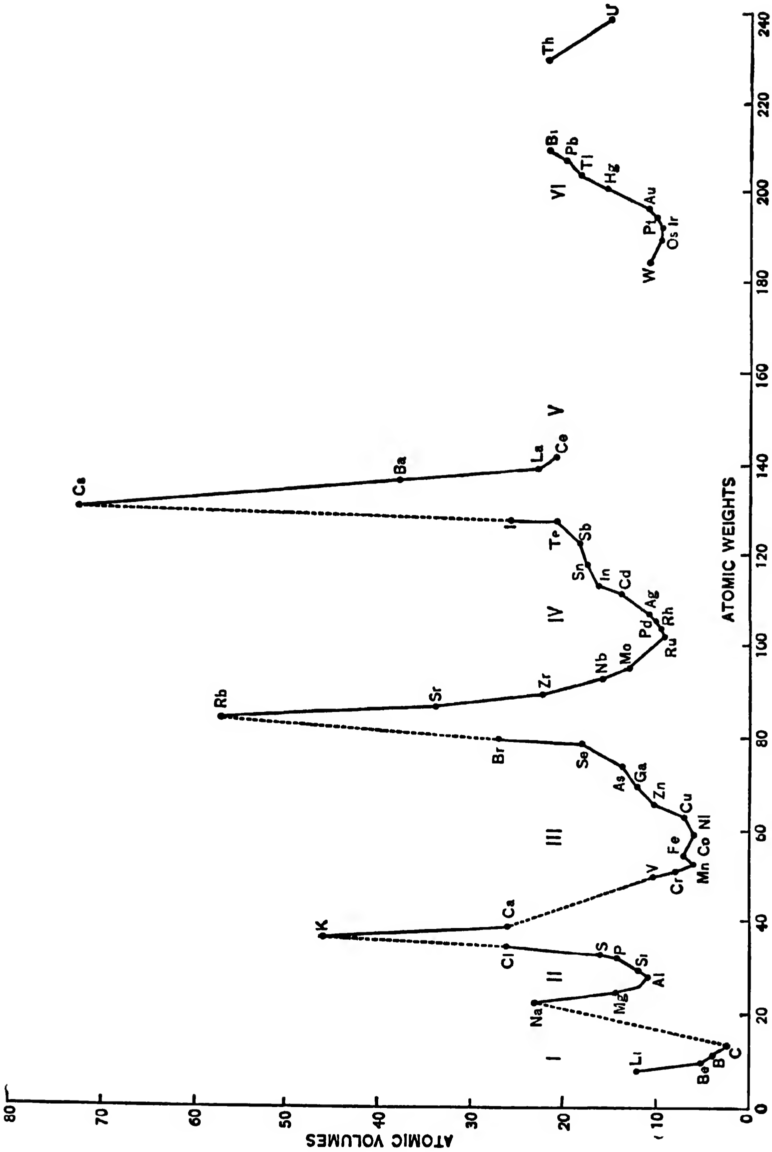

ATOMIC VOLUMES
ATOMIC WEIGHTS
0
10
20
30
40
50
60
70
80
100
120
140
160
180
200
220
240
I
II
III
IV
V
VI
Li
Be
B
C
Na
Mg
Al
Si
P
S
Cl
K
Ca
V
Cr
Mn
Fe
Co
Ni
Cu
Zn
Ga
As
Se
Br
Rb
Sr
Zr
Nb
Mo
Ru
Rh
Pd
Ag
Cd
In
Sn
Sb
Te
I
Cs
Ba
La
Ce
W
Os
Ir
Pt
Au
Hg
Tl
Pb
Bi
Th
U

Fig. 25.

the atomic volume decreases and increases regularly. The curve presents five maxima, at which we find the five alkali metals,—lithium, sodium, potassium, rubidium, and cæsium. At the minima fall those elements whose atomic weights are approximately the mean between the atomic weights of the element at the preceding and succeeding maxima. In fact, at the third, fourth, and fifth minima we find the elements which do not fit into Mendeléeff's table, and are placed by themselves in group VIII. We see also in this curve the distinction between the short and long periods of Mendeléeff's table. The first loop of the curve contains the first short period, or the elements from lithium to fluorine; the double loop from sodium to nickel the first long period, and so on. It sometimes occurs that elements with similar chemical properties have very nearly the same atomic volumes, as with chlorine, bromine, and iodine.

It is quite remarkable that for elements with very nearly the same atomic volumes, the properties are markedly different, depending upon whether the element is on an ascending or a descending arm of the curve; and, therefore, upon whether the element with the next higher atomic weight has a larger or smaller atomic volume than its own; *e.g.* phosphorus and magnesium, chlorine and calcium. If we follow the curve from its origin, we find the most strongly base-forming elements at the maxima, and the remainder on the descending arms of the curve. The acid-forming elements are on the ascending arms of the curve. Relations between a number of physical properties and atomic volumes have been pointed out. These include refraction of light, specific heat, power to conduct heat and electricity, magnetic properties, etc.

Old Atomic Weights corrected and New Elements predicted by Means of the Periodic System.—A scientific theory to be of the highest value must not simply be able to account for all the facts known, but must suggest new possibilities which were not realized when the theory was first announced. The Periodic Law has fulfilled the latter condition in a beautiful way. By means of it a number of erroneous atomic weights were corrected. The atomic weight of indium was supposed to be 75.6, and the composition of the oxide, InO. This would place it in the Periodic System between arsenic and selenium. The chemical properties and atomic volume showed that it belonged rather between cadmium and tin. Meyer gave it the atomic weight 113.4 ($75.6 \times 1\frac{1}{2}$), and regarded the oxide as having the composition In_2O_3. This was confirmed by Bunsen from specific heat determinations. The atomic weight of beryllium was thought to be 4.54, or $4.54 \times 2 = 9.08$, or $4.54 \times 3 = 13.62$. The

chemical and physical nature of the element showed that it must come between lithium and boron, and, indeed, be the head of the magnesium-calcium group. The true atomic weight was subsequently shown to be 9.1. Similarly, uranium was supposed to have the atomic weight 60, 120, or 180, and it was difficult to decide between these values. But it was probably close to 240 in terms of the Periodic System; and this conjecture has also been verified. It should be observed that in these cases the vapor-density method of determining the number of atoms in the molecule could not be employed.

The Periodic System has been used not simply to decide between an atomic weight and a multiple of this quantity, but to actually correct atomic weights imperfectly determined. Bunsen found the atomic weight of cæsium to be 123.4. This value was smaller than would be expected from the Periodic System. The correct atomic weight of cæsium was found later to be 132.9, which is in perfect accord with the system. More recent work in connection with osmium, iridium, platinum, and gold make it very probable that the order for these four elements suggested by the system is the correct one, and that the earlier determinations of atomic weights contain considerable error.

The prediction of the existence of unknown elements and the nature of their properties has been so beautifully verified in a number of cases that this has become the most striking application of the Periodic Law. Mendeléeff recognized that the atomic weight and other properties of an element can be determined from the properties of the two neighboring elements in the same series and the two neighboring elements in the same half of the same group. The properties are as a rule the mean of those of the four elements. These four elements were termed by Mendeléeff the *Atomic Analogues* of the element in question. This will be clear from the following example: —

	Ca 40	
Rb 85	Sr 88	Yt 89
	Ba 137	

The atomic weight of strontium is the mean of the atomic weights of its four analogues, and the same holds in general for the other properties.

On the basis of this fact Mendeléeff predicted the existence and properties of a number of elements which had not been discovered when the Periodic Law was announced. The element predicted was named from the element in the same group which immediately precedes it, adding the prefix "eka." In the third group the element immediately following boron was unknown, and was termed *ekaboron.* Since it followed calcium with an atomic weight of 40, and preceded titanium whose atomic weight is 48, its atomic weight must be 44. The oxide must have the composition Eb_2O_3, and bear the same relation to aluminium oxide that calcium oxide does to magnesium oxide. The sulphate must be less soluble than aluminium sulphate, just as calcium sulphate is less soluble than magnesium sulphate. The carbonate would be insoluble in water. The salts would be colorless and form gelatinous precipitates with potassium hydroxide and carbonate, and disodium phosphate. The sulphate would yield a double salt with potassium sulphate. Few of the salts would be well crystallized. The chloride would probably be less volatile than aluminium chloride, since titanium chloride boils higher than silicon chloride, and calcium chloride is less volatile than magnesium chloride. The chloride would be a solid, its volume about 78, and its density about 2. The specific gravity of the oxide would be about 3.5, and its volume about 39. Ekaboron would be a light, non-volatile, difficultly fusible metal, which would decompose water only on warming; would dissolve in acids with evolution of hydrogen, and would have a specific gravity of about 3.

In a similar manner Mendeléeff predicted the existence and properties of an element between aluminium and indium, terming it *ekaaluminium.* The atomic weight would be approximately 68.

Again, an element should exist between silicon and tin, and this was termed *ekasilicium,* with an atomic weight of 72.

The properties of the last two elements and their compounds are described in considerable detail from the properties of their atomic analogues, but for these the original paper must be consulted.

These elements have now all been discovered. The element described by Nilson as scandium, proved to be ekaboron, having an atomic weight of 44.1. Gallium, discovered by Lecoq de Boisbaudran, was the predicted ekaaluminium, with an atomic weight of 70. And germanium, discovered by Winkler, proved to be the ekasilicon, having an atomic weight of 72.5. The properties of these elements

and their compounds corresponded about as closely with the properties predicted for them as the atomic weights.

Imperfections in the Periodic System. — While admiring the many deep-seated relations which are brought out by the Periodic System, we must not fail to observe that it is far from complete. At the very outset there is evidence of this incompleteness — hydrogen does not fit at all into the scheme, and yet it is one of the most important elements. In the very first group of the elements, again, there is apparent inconsistency. Along with lithium, potassium, rubidium, and cæsium, we find copper, silver, and gold. There is evidently no very close connection between the last three elements and the first four. Further, sodium does not fall into the same division of the group with the other strongly alkaline metals, but with copper, silver, and gold. It is at once apparent that sodium is not as closely allied to these elements as to the alkali metals which constitute the other division of group I.

Passing over the intermediate groups, which contain a number of more or less serious inconsistencies, we find in group VII manganese placed with the halogens and not falling into the same group either with chromium or with iron. The relations of manganese to the halogens are not more striking than the differences, and we do not find manganese falling into the same division of the group with chlorine, bromine, and iodine, but with fluorine, to which it bears a much less close resemblance than to the remaining halogens.

When we come to group VIII, we find nothing but discrepancies. These elements do not fit into the system at all, and are placed by themselves as a separate group. It is questionable whether it is desirable to call this group VIII, since it is in no chemical or physical sense a true extension of the system one step beyond group VII. Take as an example the power of the elements to combine with oxygen. There is a regular increase in this power from unity in group I, through the several groups up to group VII, — where we find the compounds Cl_2O_7, Br_2O_7, I_2O_7, — fluorine not combining at all with oxygen. Of all the elements in the so-called group VIII, there is only one, osmium, which has a valence of eight towards oxygen. The remainder all show a lower valence towards this element.

It seems better to recognize these elements as distinct exceptions, which do not fit into the Periodic System at all satisfactorily; yet even here we must recognize a certain periodicity in the recurrence of these exceptions, and that they occur in every case in groups of three. The Periodic System seemed to be hard pressed for a time to find a place for some of the elements described by Ramsay as occur-

ring in the atmospheric air. Quite recently, however, Ramsay has shown that these elements have a place in the Periodic System. These apparent discrepancies in the Periodic System have not been pointed out with the desire to undervalue the merits of this important generalization, but simply to arrest attention to the fact that the system is still far from complete. What has already been accomplished is of tremendous importance, as is shown by the single fact that we can correct atomic weights and predict the properties of elements entirely unknown. Indeed, we can do more; we can predict with what elements the unknown element in question would form compounds, the composition of these compounds, and even the color and other physical properties possessed by them.

We shall probably never have a complete and perfect Periodic System of the elements until our knowledge of these substances and their compounds is far deeper than at present. If the system was perfect and complete, it is more than probable that it would lose some of the interest which it now possesses; since it would then offer far less incentive to investigation, which is one of the best tests of the scientific value of any theory or generalization.

General Scheme to be Followed. — In dealing with the remaining elements we shall be guided largely by the Periodic System. This system, however, is, as we have seen, defective, and we shall, therefore, not follow it blindly, but depart from it whenever the relations can be more clearly established by doing so.

We shall begin with the members of group VII in Mendeléeff's table, omitting, however, one member, manganese, which will not be taken up until much later.

We shall then take up some of the members of group VI — sulphur, selenium, and tellurium; while chromium, molybdenum, tungsten, and uranium will not be studied until very much later. The nitrogen group (V) will then be studied, and following this the carbon group (IV).

The metallic elements will then be taken up. Groups I and II will be studied very nearly in the order indicated in the Periodic System, while the remaining metallic elements will be studied more or less independent of the system.

CHAPTER XI

BROMINE, IODINE, FLUORINE

BROMINE (At. Wt. = 79.96)

Occurrence and Preparation. — The element bromine, which was discovered by Balard in 1826, and named from its bad odor, closely resembles the element chlorine. Like the latter it does not occur in the free condition in nature, and occurs in very much smaller quantity than chlorine. The compounds of bromine, like those of chlorine, being in general very soluble, the chief occurrence of bromine is in the waters of the sea. Where sea-water has evaporated and deposited the great salt beds of the earth we find the bromides mixed with a large number of other salts. Among these should be mentioned especially the great deposits at Stassfurt in Germany, from which much of the bromine of commerce is obtained. Bromine also occurs in combination with metals as bromides, in many of the mineral springs of central Europe and Ohio.

Bromine is prepared by three methods: The electrolysis of bromides, which is strictly analogous to the electrolysis of chlorides, the bromine ion passing to the anode and separating in the free condition, while the metal passes to the cathode.

A second method which was much used formerly, but is now seldom employed on a large scale, consists in the oxidation of hydrobromic acid by manganese dioxide; the hydrobromic acid being set free from the bromide by means of sulphuric acid.

$$2\,NaBr + H_2SO_4 = Na_2SO_4 + 2\,HBr;$$
$$2\,HBr + MnO_2 + H_2SO_4 = MnSO_4 + 2\,H_2O + Br_2.$$

Combining these in one equation, we have: —

$$2\,NaBr + MnO_2 + 2\,H_2SO_4 = MnSO_4 + Na_2SO_4 + 2\,H_2O + Br_2.$$

The third method consists in the replacement of bromine from bromides by means of chlorine.

$$2\,KBr + Cl_2 = 2\,KCl + Br_2.$$

This method finds extensive use to-day.

Chemical Properties of Bromine. — Bromine in its chemical propperties strikingly resembles chlorine. Like the latter it unites directly with most of the elements. The compounds formed — the bromides — are not as stable as the chlorides. This is shown by the fact that chlorine replaces bromine from the bromides. The bromides, like the chlorides, are in general soluble in water, the bromides being more soluble than the chlorides. In solvents other than water, such as the alcohols, etc., the bromides are almost always more soluble than the chlorides.

Bromine has a remarkable power to disintegrate organic substances. Like chlorine it replaces the hydrogen in such compounds, and effects even deeper transformations. Its action upon the mucous membrane of the throat and nose is much more vigorous than that even of chlorine, and great precaution must, therefore, be taken in working with this substance, to be protected from its disintegrating fumes. A bottle containing bromine should never be opened except under a hood with good ventilation.

Detection of Bromine. — The chemical properties of bromine are so closely allied to those of chlorine that it might at first sight seem difficult to determine with which we are dealing, especially if it is combined with other substances. This difficulty is, however, only apparent. If a bromide is treated with chlorine, the bromine, as we have seen, is set free and can be recognized by its odor and color. If a solution of a bromide is treated with a little chlorine water, a little carbon disulphide being added to the tube and shaken vigorously, the bromine which has been set free by the chlorine is dissolved by the carbon disulphide and imparts its characteristic reddish-brown color to the solution.

Again, if we add a solution of silver nitrate to a solution of a bromide, the bromine ion combines with the silver ion, forming silver bromide, which is practically insoluble in water. Silver bromide, however, is white like silver chloride, and the eye could not distinguish between them. It might, therefore, seem difficult to determine whether we were dealing with a chloride or a bromide. Such, however, is not the case, since silver chloride readily dissolves in ammonia, while silver bromide is much less soluble. When we have a precipitate formed which we know is either silver chloride or silver bromide, it is only necessary to add a few drops of ammonia. If the precipitate dissolves it is the chloride, if it does not disappear in solution it is the bromide. In making this test care must be taken not to add much ammonia water, since silver bromide is soluble also in a large amount of ammonia.

Bromine Atoms and Bromine Ions. — Bromine in the atomic condition behaves very differently from bromine in the ionic condition. We have just seen how the bromine ions behave when brought in contact with the silver ions. They combine with them at once, forming the characteristic precipitate, silver bromide.

$$\overset{+}{K}, \overset{-}{Br} + \overset{+}{Ag}, \overset{-}{NO_3} = \overset{+}{K}, \overset{-}{NO_3} + AgBr.$$

When bromine in the unionized condition is brought into the presence of silver ions, it does not combine to the slightest extent with the silver ions. Thus, bromine in such compounds as ethyl bromide, C_2H_5Br, is not in the ionized condition. It is presumably in the atomic condition, forming a part of the undissociated molecule of the non-electrolyte, ethyl bromide. Bromine in this condition does not react with a solution of silver nitrate — with silver ions.

Physical Properties of Bromine. — The reddish-brown liquid, bromine, has a density of 3.1. It boils at 63°, yielding a reddish-yellow vapor. The density of the vapor is 160 in terms of hydrogen as two, provided the bromine vapor has not been heated above 300°. The atomic weight being 80, the molecule of bromine therefore contains two atoms, or has the composition represented by the formula Br_2. If the vapor of bromine is heated above 300°, the density becomes less as the temperature is raised, showing that the molecules of Br_2 are gradually breaking down into molecules of Br.

Bromine solidifies at − 7°, forming an orange-red solid. A beautiful experiment consists in introducing some bromine into a flask with a narrow neck, and drawing the neck out to a fine tube. The tube is sealed, and is then full of bromine vapor. Upon the bottom of the flask place some solid carbon dioxide and ether, or, still better, a little liquid air. At these extremely low temperatures the bromine solidifies at once from the spot on the glass where the solid carbon dioxide or the liquid air was placed.

Bromine dissolves in water, forming what is known as *bromine water*, which is analogous to chlorine water. The saturated solution in water contains about 3 per cent of bromine. When a solution of bromine water is exposed to the light, hydrobromic acid is formed and oxygen is liberated, just as when a solution of chlorine water is exposed to the light hydrochloric acid is formed and oxygen is liberated. Bromine forms a hydrate with cold water analogous to chlorine hydrate, but bromine hydrate is more stable than chlorine hydrate. The composition of bromine hydrate is apparently $Br_2 + 10\,H_2O$, but this seems to change with the conditions. Bromine is extensively used in connection with photography and with medicine.

Hydrobromic Acid, HBr. — When hydrogen and bromine are mixed and the mixture subjected to an electric spark or exposed to the light, the elements do not combine with explosive violence as was the case with chlorine and hydrogen. They do combine, however, to a certain extent, forming hydrobromic acid. The amount of combination can be greatly increased by passing the mixed gases over finely divided, hot platinum, which acts catalytically upon the mixture.

Hydrobromic acid can be prepared by the action of bromine upon compounds containing carbon and hydrogen. The bromine displaces a part of the hydrogen, combining with it and forming hydrobromic acid. When bromine acts upon benzene the following reaction takes place: —

$$C_6H_6 + 2\,Br_2 = C_6H_4Br_2 + 2\,HBr.$$

The best method, however, of preparing hydrobromic acid is by allowing water to act upon the bromides of certain acid-forming elements such as phosphorus. The reaction that takes place in this case is —

$$PBr_5 + H_2O = POBr_3 + 2\,HBr,$$

resulting in the formation of phosphorus oxybromide and hydrobromic acid.

A method which was formerly used, but which is far less satisfactory than that just described, consists in treating phosphorus with bromine in the presence of water. The phosphorus and bromine combine, forming the tribromide or pentabromide of phosphorus, depending upon the amount of bromine used. If the tribromide is used, the reaction which takes place is the following: —

$$PBr_3 + 3\,H_2O = \underset{\text{[Phosphorous acid]}}{H_3PO_3} + 3\,HBr.$$

If the pentabromide is formed, the decomposition with water takes place as represented by the above equation, or if more water is added the oxybromide is decomposed into hydrobromic acid and phosphoric acid, thus: —

$$POBr_3 + 3\,H_2O = H_3PO_4 + 3\,HBr.$$

The question which would naturally be asked is why not prepare hydrobromic acid by the action of sulphuric acid on bromides? This would be analogous to the preparation of hydrochloric acid by the action of sulphuric acid on chlorides.

This method is theoretically possible, but precaution must be taken or a secondary reaction between the hydrobromic acid formed and the sulphuric acid takes place, which interferes with the value of the method.

If the sulphuric acid is dilute, the hydrobromic acid formed dissolves in the aqueous sulphuric acid on account of its great solubility in water. If, on the other hand, the sulphuric acid used is concentrated, the following reaction takes place: —

$$H_2SO_4 + 2\,HBr = 2\,H_2O + SO_2 + Br_2.$$

The hydrobromic acid is oxidized to bromine by the sulphuric acid, which is reduced to sulphur dioxide.

Properties of Hydrobromic Acid. — Hydrobromic acid resembles hydrochloric acid very closely in its chemical and physical properties. It is a colorless gas with penetrating odor, very soluble in water. An aqueous solution saturated at zero contains about 80 per cent of the acid. Such solutions give off dense fumes when exposed to the air, or when the breath is blown across the mouth of the flasks which contain them.

Hydrobromic acid is a reducing agent, as we have seen in its action on sulphuric acid. It is also a very strong acid. A dilute, aqueous solution of hydrobromic acid is completely dissociated into its ions: —

$$HBr \rightleftharpoons \overset{+}{H}, \overset{-}{Br}.$$

The bromine ions manifest their presence by combining with the silver ions when brought in contact with them, forming the white precipitate, silver bromide, which is soluble with difficulty in ammonia.

When chlorine is brought into the presence of a bromide, as we have seen, or of hydrobromic acid, the bromine separates and chlorine passes into solution. If we examine this reaction more closely, we find that what has taken place is a transfer of the electrical charge from the bromine ion to the chlorine atom, converting the latter into an ion, while the bromine ion having lost its charge is converted into an atom. The atoms of bromine then combine and form the molecules of bromine. The reaction which takes place would be represented thus: —

$$\overset{+}{H}, \overset{-}{Br} + Cl = \overset{+}{H}, \overset{-}{Cl} + Br.$$

This action of chlorine on hydrobromic acid is analogous to the action of metals on acids in general. In the former case we have a transfer of the negative charge from the anion bromine to the chlorine, converting the bromine into an atom, and the chlorine into an anion. In the latter case the positive charge is transferred from the cation hydrogen to the metal, converting the hydrogen into an atom and the metal into a cation. The main difference between the two re-

actions is that in one case we have a transfer of the negative charge, in the other case a transfer of the positive charge.

When a concentrated solution of hydrobromic acid in water is cooled sufficiently, a crystalline hydrate separates having the composition $HBr.2H_2O$.

Hydrobromic acid gas can be liquefied. It boils at $-73°$ and solidifies at $-87°$.

Compounds of Bromine with Oxygen and Hydrogen. — Bromine forms two well-characterized acids with oxygen and hydrogen. These are hypobromous and bromic acids. While hydrobromic acid is less stable than hydrochloric, as we have seen, oxygen acids of bromine are more stable than the corresponding acids of chlorine.

When bromine is conducted into water in the presence of mercuric oxide, *hypobromous acid* is formed: —

$$HgO + 2\,Br_2 + H_2O = HgBr_2 + 2\,HBrO.$$

The acid resembles very strikingly hypochlorous acid. Like the latter it gives up its oxygen readily, being, therefore, a good oxidizing agent.

The sodium salt of hypobromous acid is prepared by the action of bromine on sodium hydroxide: —

$$2\,NaOH + 2\,Br = H_2O + NaBr + NaOBr.$$

This method of preparing sodium hypobromite is strictly analogous to the method of preparing sodium hypochlorite.

Bromic Acid, $HBrO_3$, is prepared by oxidizing bromine by means of chlorine monoxide, also by fusing bromides with chlorates; the bromide being converted into the bromate and the chlorate into the chloride.

The best method, however, of preparing bromic acid, is by the action of bromine on caustic potash. A mixture of potassium bromide and bromate is formed: —

$$6\,KOH + 3\,Br_2 = 5\,KBr + KBrO_3 + 3\,H_2O.$$

From this mixture the potassium bromate can be readily separated by *fractional crystallization*, — the same method which was employed to separate potassium chlorate from potassium chloride. The bromate is much less soluble in water than the bromide, and readily crystallizes from a not too dilute solution of the two salts in water.

Bromic acid is obtained from potassium bromate by methods strictly analogous to those employed for obtaining chloric acid from potassium chlorate, by treating barium bromate with dilute sul-

phuric acid, or silver bromate with dilute hydrochloric acid. The barium sulphate, or silver chloride formed, is insoluble and can be readily filtered off from the solution of bromic acid.

The bromine analogue of perchloric acid — perbromic acid — does not exist.

No compounds of oxygen and bromine have been made. If they are formed they are too unstable to be isolated.

Compound of Bromine with Chlorine, BrCl. — Bromine combines with chlorine, forming one compound, bromine chloride, having the composition BrCl. It is formed when cold chlorine gas is conducted into liquid bromine. It is a reddish-brown liquid, which decomposes at 10°.

It is rather surprising that this compound should exist, when we consider how closely allied chlorine and bromine are in their chemical properties; it being a general rule that the more closely related elements are the least liable to enter into chemical combination.

IODINE (At. Wt. = 126.85)

Occurrence and Preparation. — Iodine, which was discovered by Courtois in 1812, and named from the violet-blue color of its vapor, occurs very rarely in the free condition. It is widely distributed in nature, occurring, however, usually only in small quantities. It occurs along with chlorides and bromides, but in very much smaller quantities than either of these substances. It also occurs in sea-water, as we would expect, on account of the solubility of its compounds. It is taken up from the waters of the sea by certain sponges and plants, and exists in considerable quantity in the ashes of such plants. It occurs also in certain ores, especially those of silver, and in the deposits of soda saltpetre in Chili and Peru. It also occurs in small quantity in deposits of rock-salt.

Iodine is obtained to-day mainly from *Chili saltpetre*, in which it occurs in the form of sodium iodate. The iodine is obtained from this salt by reduction with sulphurous acid: —

$$2\,NaIO_3 + 5\,H_2SO_3 = 4\,H_2SO_4 + Na_2SO_4 + H_2O + I_2.$$

The sulphurous acid is oxidized to sulphuric acid, the iodate being reduced and iodine set free.

There are other methods of obtaining iodine, such as the oxidation of hydriodic acid by one or another oxidizing agents.

$$4\,HI + O_2 = 2\,H_2O + 2\,I_2.$$

The agent most frequently used is manganese dioxide. When an iodide is treated with manganese dioxide and sulphuric acid the following reaction takes place:—

$$2\,KI + MnO_2 + 2\,H_2SO_4 = MnSO_4 + K_2SO_4 + 2\,H_2O + I_2.$$

Iodine can also be displaced from iodides by means of chlorine. When a solution of potassium iodide is treated with chlorine water the following reaction takes place:—

$$\overset{+}{K}\,,\,\overset{-}{I} + Cl = \overset{+}{K}\,,\,\overset{-}{Cl} + I.$$

This is analogous to the action of chlorine upon bromides, which we have seen consists in a transferrence of the electrical charge from the bromine ion to the chlorine. Here we have the charge transferred from the iodine ion to the chlorine, which becomes an ion, the iodine having lost its charge becoming an atom.

Chemical Properties of Iodine.—The purplish-black solid, iodine, resembles strongly in its chemical properties the elements chlorine and bromine. It combines with many other elements, but is not quite as active chemically as bromine and chlorine. Bring together a few flakes of iodine and a small piece of dry phosphorus in a porcelain dish. Combination between the two will take place at once, resulting in the formation of an iodide of phosphorus. Iodine, like bromine and chlorine is a strong oxidizing agent. When brought in contact with substances which can take up oxygen in the presence of water, it takes the hydrogen from the water forming the compound hydriodic acid, with which we shall soon become familiar; and the oxygen is taken up by the oxidizable substance. Thus, when iodine is brought in contact with the easily oxidizable compound sulphurous acid, its color disappears rapidly and the iodine passes into solution as hydriodic acid.

$$H_2SO_3 + H_2O + I_2 = H_2SO_4 + 2\,HI.$$

The oxidizing power of iodine is frequently made use of to determine the quantity of this substance present.

Detection of Iodine.—Iodine forms a characteristic blue color with starch paste, which enables its presence to be easily detected. The starch paste must be carefully prepared in order that the reaction may be sensitive. Some granules of starch should be placed in a porcelain mortar and a little cold water added. The starch should be ground with the water to a fine paste. The paste should be poured into a beaker, and hot (not boiling) water added in considerable quantity with vigorous stirring. Under these conditions some

of the starch dissolves in the water. After the solution has stood for a time the supernatant liquid is poured off, and is then ready to be used in detecting iodine. This reaction is so sensitive that it can be used to detect a mere trace of free iodine.

If the iodine is combined as in the iodide of a metal, it can be detected by simply adding concentrated sulphuric acid. The hydriodic acid set free reacts with the sulphuric acid reducing it, and the iodine is liberated as such. It can be recognized by the characteristic dark-brown color which it imparts to the solution.

Detection of Iodine in the Presence of Bromine and Chlorine. — We have seen that iodine resembles closely in its chemical behavior both bromine and chlorine. The question arises, How can iodine be detected in the presence of one or both of these closely related elements? There are several methods by which this can be effected.

If to a solution containing an iodide, bromide, and chloride, a little chlorine water is added, the iodine will separate first. If a little carbon disulphide is added and vigorously shaken with the solution, it will dissolve the free iodine and acquire the characteristic purplish-red color of this substance. In detecting iodine by this method care must be taken to add the chlorine water drop by drop and not in excess. If an excess of chlorine is introduced, it will cause the free iodine to be oxidized to iodic acid, which we shall study a little later, and which is colorless.

If, after the iodine has separated, more chlorine water is added to the solution, the iodine color will disappear for the reason indicated above, and free bromine will then begin to separate, which will give its characteristic reddish-brown color to the carbon disulphide. It is thus possible to detect iodine in the presence of bromine and chlorine, and also bromine in the presence of the other two substances.

Another method for detecting these three closely related elements is based upon the different solubilities of the three silver salts in ammonia. We have seen that silver chloride is very easily soluble in ammonia, and that silver bromide is soluble with difficulty. Silver iodide is insoluble in ammonia, or soluble to only such a slight extent that it is practically insoluble. Further, while silver chloride and bromide are white, silver iodide is yellow.

If to a solution containing the three substances, chloride, bromide, and iodide, silver nitrate is added in excess, we will have the three salts of silver — chloride, bromide, and iodide — precipitated. The precipitates are now filtered off and treated with a few drops of dilute ammonia. If any appreciable quantity of the precipitate dissolves,

this is silver chloride. Enough ammonia is now added to the precipitates to dissolve all of the silver chloride. If on further addition of a considerable volume of ammonia more of the precipitate dissolves, this would mean that we had bromine present. If a yellowish precipitate remains behind which is insoluble in ammonia, this is silver iodide.

In determining whether, under any given conditions, a part of the precipitate has dissolved in the ammonia, a little nitric acid is added to the ammoniacal solution. Any precipitate held in solution by the ammonia would be again precipitated.

Physical Properties of Iodine. — Although iodine is a solid at ordinary temperatures, it can readily be converted into vapor at a slightly elevated temperature. When iodine is heated exposed to the air, *i.e.* under ordinary conditions, it does not melt, but passes at once into vapor. It can, however, be melted at 114°, and boils at 184°.

The vapor-density of iodine between 200° and 600° is such as to show that the molecular weight is 256. Since the atomic weight is 126.85, the molecule of iodine at these temperatures consists of two atoms. As the temperature rises, the German chemist, Victor Meyer, has shown that the vapor-density decreases, and that above 1400° the density is only about one-half the value at the lower temperature. Above 1600° it is quite certain that the vapor-density of iodine would remain constant, since at this temperature the atom and molecule would be identical, and no further dissociation of the molecules could take place.

The vapor of iodine can be readily condensed to a solid when the temperature of the vapor is again lowered. This process of converting a solid into a vapor, and recondensing the vapor to a solid, is known as *sublimation*. The best method of purifying iodine is to sublime it. The impurities, being for the most part non-volatile at the temperature at which iodine volatilizes, remain behind in the solid form.

Iodine dissolves in water to only a slight extent. If to the water potassium iodide or hydriodic acid is added, the solution dissolves iodine in considerable quantities. Iodine dissolves readily in carbon disulphide, chloroform, alcohol, and ether. Solutions of iodine in the last two solvents are known as *tincture of iodine*.

Hydriodic Acid, HI. — When a mixture of hydrogen and iodine is heated, there is partial combination between the two forming hydriodic acid, HI. Only a portion of the mixture, however, combines. The *velocity of the reaction*, *i.e.* the amount of hydriodic acid which

is formed in a given time can be greatly increased by heating the mixture in the presence of finely divided platinum, which acts by contact, or *catalytically*, as we say. Even under these conditions a complete combination of the two gases cannot be effected.

A far more convenient method of preparing hydriodic acid is by the action of water on phosphorus triiodide, PI_3: —

$$PI_3 + 3\,H_2O = H_3PO_3 + 3\,HI,$$

or by the action of iodine on phosphorus in the presence of water: —

$$3\,I + P + 3\,H_2O = H_3PO_3 + 3\,HI.$$

Hydriodic acid cannot be prepared by the action of sulphuric acid on iodides, since, as we have seen, hydriodic acid reduces sulphuric acid. The extent to which this reduction takes place depends largely upon the temperature and concentration of the solutions. If the solutions are cold and dilute, the reduction of the sulphuric acid may only proceed as far as sulphur dioxide, —

$$H_2SO_4 + 2\,HI = I_2 + 2\,H_2O + SO_2.$$

If the solutions are more concentrated and warmer, we may have free sulphur formed: —

$$H_2SO_4 + 6\,HI = 3\,I_2 + 4\,H_2O + S.$$

If the solutions are still more concentrated and hot, the reduction may proceed still farther and give us, from the sulphuric acid, hydrogen sulphide, — the lowest reduction product of sulphuric acid.

$$H_2SO_4 + 8\,HI = 4\,I_2 + 4\,H_2O + H_2S.$$

Hydriodic acid is in general a strong reducing agent, readily giving up its hydrogen to substances which can take it, or taking oxygen from substances which can lose it. This is due to the ease with which hydriodic acid is broken down, or *dissociated by heat*, into hydrogen and iodine.

The gas, hydriodic acid, is readily liquefied. At 0° a pressure of four atmospheres is sufficient to convert the gas into a liquid. The liquid is readily solidified, the solid melting at — 51°.

The gas dissolves very readily in water, one volume of water dissolving, at 0°, about 500 volumes of the acid. There is a solution of hydriodic acid and water which has a constant boiling-point. This contains 57 per cent of acid and boils at 126°. This is analogous to the constant boiling mixture of hydrochloric acid and water. Like the latter, also, it is not a definite chemical compound, since its

composition can be changed by varying the pressure under which it is boiled.

An aqueous solution of hydriodic acid quickly turns brown when allowed to stand exposed to the air. This is due to the oxidation of the acid by the oxygen of the air, and the consequent liberation of iodine.

We have seen that iodine dissolves far more readily in a solution of an iodide, or hydriodic acid, than in pure water, — in a word, in a solution already containing a large number of iodine ions. We can now see a reason for this rather remarkable fact. The iodine combines with the iodine ion, already in the solution, forming the complex ion, $\bar{I}_3$, which is brown, while the iodine ion, $\bar{I}$, is colorless. This complex ion, $\bar{I}_3$, gives its characteristic brown color to the solution.

Compounds of Iodine with Oxygen and Hydrogen. — Iodine forms two well-characterized compounds with oxygen and hydrogen. These are *iodic acid* and *periodic acid*. When iodine is dissolved in caustic potash the reaction takes place thus: —

$$6\,KOH + 3\,I_2 = 5\,KI + KIO_3 + 3\,H_2O.$$

It is probable that during this reaction potassium hypoiodite is formed. If so, this is so unstable that it breaks down into iodide and iodate.

The iodates are more readily prepared by the action of iodine on chlorates in the presence of water.

$$5\,KClO_3 + 3\,I_2 + 3\,H_2O = 5\,KIO_3 + HIO_3 + 5\,HCl.$$

When no water is present we have: —

$$KClO_3 + I = KIO_3 + Cl.$$

When potassium iodate is treated with barium chloride, barium iodate, which is difficultly soluble, is formed, and potassium chloride, in accordance again with the general principle, that whenever an insoluble, or difficultly soluble compound can be formed, it is formed.

$$2\,KIO_3 + BaCl = Ba(IO_3)_2 + 2\,KCl.$$

When barium iodate is treated with a dilute solution of sulphuric acid the following reaction takes place: —

$$Ba(IO_3)_2 + H_2SO_4 = BaSO_4 + 2\,HIO_3,$$

barium sulphate being much more insoluble than barium iodate.

This is the best method of preparing iodic acid.

Iodic acid is a well-crystallized compound, soluble in water, and a very strong acid.

It may dissociate thus:—

$$HIO_3 = \overset{+}{H}, \overset{-}{IO_3},$$

or thus: $$2\,HIO_3 = \overset{+}{H}, H(\overset{-}{IO_3})_2,$$

or thus: $$3\,HIO_3 = \overset{+}{H}, H_2(\overset{-}{IO_3})_3,$$

shown by the fact that we have salts of the following compositions:—

$$MIO_3,\ MH(IO_3)_2, \text{ and } MH_2(IO_3)_3.$$

When iodic acid is carefully heated above 100°, it loses water and passes over into a white powder, *iodine pentoxide*,—

$$2\,HIO_3 = H_2O + I_2O_5.$$

Iodine pentoxide dissolves in water, combining with it and forming again iodic acid. Iodic acid and iodine pentoxide readily give up their oxygen, and are, therefore, good oxidizing agents.

When the salts of iodic acid are heated or subjected to the action of strong oxidizing agents, they pass over into the salts of periodic acid.

Periodic acid does not have a composition strictly analogous to perchloric or perbromic acid, but this plus two molecules of water:—

$$\underset{\text{(unknown)}}{HIO_4} + 2\,H_2O = H_5IO_6.$$

The acid is best prepared by transforming the acid sodium salt, $Na_2H_3IO_6$, into the acid silver salt, $Ag_2H_3IO_6$, the acid sodium salt being prepared by conducting chlorine gas into a boiling solution of sodium iodate to which sodium carbonate has been added.

When the silver salt, $Ag_2H_3IO_6$, is decomposed with water it yields periodic acid, H_5IO_6, and the silver salt of this acid, Ag_5IO_6:—

$$5\,Ag_2H_3IO_6 = 2\,Ag_5IO_6 + 3\,H_5IO_6.$$

Periodic acid, H_5IO_6, is easily soluble in water, and when gently heated loses water and passes over into *iodine septoxide*, I_2O_7. When heated to 140°, periodic acid loses oxygen as well as water, and passes over into iodide pentoxide, I_2O_5.

Some of the periodates indicate that the composition of periodic acid is HIO_4, others that the acid has the composition, H_3IO_5, and others still that the acid is H_5IO_6. These facts, however, are not

inconsistent. One of these acids is easily derived from the others by the addition or subtraction of water: —

$$HIO_4 + H_2O = H_3IO_5,$$
$$H_3IO_5 + H_2O = H_5IO_6.$$

Periodic acid readily loses oxygen, and is therefore a good oxidizing agent.

Compounds of Iodine with Chlorine, ICl, ICl_3. — Iodine forms two compounds with chlorine, ICl and ICl_3. When chlorine is brought in contact with iodine in the absence of moisture, both of these compounds are formed. Iodine monochloride is a reddish-brown liquid, boiling with partial decomposition at 101°, and forming crystals which melt at 14° or 27°, depending upon the conditions of their formation. The one with the higher melting-point is the more stable form.

When an excess of chlorine is conducted over iodine, the trichloride is formed. It is a reddish-yellow solid, breaking down easily into chlorine and the monochloride. Both of these compounds are decomposed by water into iodine, hydrochloric acid, and iodic acid.

Compound of Iodine with Bromine. — Iodine forms only one compound with bromine — iodine bromide — having the composition IBr. It is an unstable solid, easily decomposed by water or by rise in temperature.

The relation pointed out earlier in the case of bromine obtains here. Iodine is more closely allied to bromine, chemically, than it is to chlorine. With the latter it forms two compounds, and with the former only one, which is very unstable. The more closely allied elements are least likely to enter into chemical combination.

FLUORINE (At. Wt. = 19.0)

Occurrence and Preparation. — Fluorine, on account of its unusual chemical activity, does not occur in nature in the free condition. It occurs mainly in combination with the element calcium as *fluor spar*, from which it derives its name. Fluor spar is so called because it readily melts and flows, serving as a flux for other substances. Fluorine also occurs in another mineral, *cryolite*, in considerable quantity. Cryolite is a double fluoride of sodium and aluminium, occurring mainly in Greenland, and having the composition Na_3AlF_6.

The problem of isolating fluorine remained for a long time unsolved. On account of the great chemical activity of this substance,

as soon as it was set free from its compounds it would combine again with whatever it came in contact. The problem of isolating fluorine was solved by the French chemist, Moissan. He electrolyzed hydrofluoric acid and obtained hydrogen at the cathode and fluorine at the anode. If there is any water present, the fluorine as rapidly as formed would act upon it and decompose it, yielding oxygen and hydrofluoric acid. An aqueous solution of hydrofluoric acid, therefore, cannot be used. Liquid hydrofluoric acid or the anhydrous gas cannot be used, since they do not conduct the electric current.

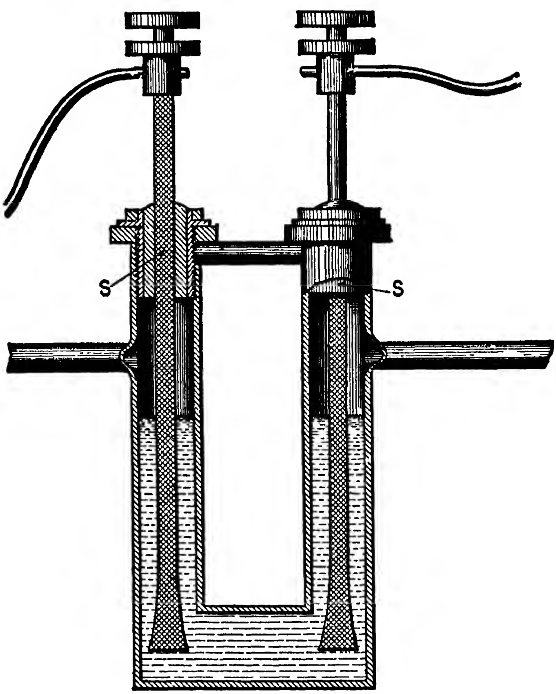


FIG. 26.

Moissan found that when potassium fluoride is dissolved in anhydrous hydrofluoric acid the solution conducts the current, hydrogen being liberated at the cathode and fluorine at the anode. At first the attempt was made to use vessels lined with calcium fluoride where the fluorine escapes, but vessels of platinum were subsequently employed and found to work very satisfactorily. Indeed, it has subsequently been shown that fluorine does not act very vigorously upon copper, and copper vessels have been used in which to liberate the element fluorine.

The apparatus used by Moissan for preparing fluorine is shown in Fig. 26. The apparatus and electrodes, made of platinum-iridium, have the form shown in the figure. The electrodes are insulated by means of stoppers (S.S.) of fluor spar. The apparatus is kept at a temperature of $-23°$ by means of methyl chloride. The fluorine, liberated on the anode, passes out through a spiral platinum tube cooled to $-50°$ by means of methyl chloride, and then through two tubes of sodium fluoride to remove all traces of hydrofluoric acid. The apparatus holds about 160 cc. The solution which is to be electrolyzed contains 20 grams of potassium fluoride dissolved in 100 grams of anhydrous hydrofluoric acid.

Chemical Properties of Fluorine. — Fluorine is one of the most active chemically of all the elements. It replaces chlorine from chlorides and from hydrochloric acid. At ordinary temperatures it combines with most of the metals, converting them into fluorides. Platinum and gold are about the only metals which resist its action, and these are transformed into fluorides at elevated temperatures.

What is more surprising, fluorine combines also with most of the metalloids, and at ordinary temperatures. The only elements which resist the action of fluorine are nitrogen, chlorine, oxygen, and argon and its associates.

When fluorine decomposes water, the oxygen which is liberated contains a large amount of ozone.

Moissan describes a number of very beautiful experiments, where the fluorine as it escapes from his apparatus is allowed to come in contact with various metallic and non-metallic elements. Many of these take fire and burn readily in a stream of fluorine, at ordinary temperatures, evolving a large amount of light and heat.

Physical Properties of Fluorine. — Fluorine is a gas at all ordinary temperatures, having a light, greenish-yellow color. It is much lighter in color than chlorine, and much more active upon the mucous membrane of the nose and throat. Its vapor-density indicates that at ordinary temperatures it is broken down in part into molecules which are identical with the atom. Its vapor seems to be composed in part of molecules of F_2 and in part of molecules of F_1.

Similar relations were observed in the cases of bromine and iodine, but only at much higher temperatures.

Fluorine has been liquefied by the combined efforts of Moissan in France, and Dewar in England. The fluorine was cooled to $-190°$ by means of liquid air, when it liquefied and was received in a glass bulb with a vacuum-jacket. Fluorine boils at $-187°$, and at this low temperature has lost much of its chemical activity, as is obvious

from the fact that it can be received in a glass vessel. Liquid fluorine does not act upon iron, and does not even replace iodine from its compounds. All attempts to solidify fluorine, except the most recent, were unsuccessful. It has recently been converted into a solid.

Hydrofluoric Acid, HF.—Hydrogen fluoride, or hydrofluoric acid, is prepared most conveniently by the action of sulphuric acid on calcium fluoride:—

$$CaF_2 + H_2SO_4 = CaSO_4 + 2\,HF.$$

The most characteristic chemical property of hydrofluoric acid is its power to act upon glass, etching it, as we say. It is extensively used for this purpose in preparing measuring apparatus especially for chemical work. Hydrofluoric acid does not act upon paraffine and similar organic substances. The glass vessel upon which it is desired to make a permanent line is covered with paraffine by dipping it into the molten material. A fine line is then drawn through the paraffine at the place where it is to appear on the glass. The glass is thus exposed at this place. It is now subjected to the action of the fumes of hydrofluoric acid. Where the glass is protected by the paraffine, it is not acted upon by the fumes of the acid. Where the paraffine has been removed, however, the glass is etched.

This can be readily tried in the laboratory by covering a watch-crystal with paraffine and scratching a line, letter, or number upon it. Then expose the glass to the action of the fumes of hydrofluoric acid. After a time remove the paraffine by dissolving it in oil of turpentine, and the crystal will be etched wherever the paraffine has been removed.

It is obvious from the above that hydrofluoric acid cannot be prepared or kept in glass bottles. It does not attack platinum vessels, and acts only slightly upon vessels of lead. It is preserved in vessels of gutta percha, upon which it acts only slightly. Hydrofluoric acid is much weaker than either hydrochloric, hydrobromic, or hydriodic acid. It is readily soluble in water, and its aqueous solution is the form in which it is nearly always employed. Like the acids mentioned above, it forms a constant boiling mixture with water, but this is not a definite compound.

The vapor-density of the pure acid would show a molecule much more complex than would be indicated by the formula HF. The composition of cryolite, Na_3AlF_6, points to the same conclusion. There are a number of examples of fluorine and the other halogens tending to form aggregates of six atoms, as in cryolite.

Fluorine differs from chlorine, bromine, and iodine in that its sil-

ver salt is readily soluble and its calcium salt insoluble. Anhydrous hydrofluoric acid boils at 19°.4, and solidifies at 92°.5.

On account of the great chemical activity of fluorine and hydrofluoric acid, they are very dangerous substances to work with, acting upon organic matter with great vigor. Special precautions must therefore be taken in dealing with them.

Compound of Fluorine with Iodine, IF_5. — One compound of fluorine and iodine is said to have been prepared. This has the composition IF_5, and is obtained by allowing iodine to act on dry silver fluoride: —

$$3\,I_2 + 5\,AgF = 5\,AgI + IF_5.$$

The compound IF_5 is known as *iodine pentafluoride.*

Comparison of the Several Acids formed by the Halogens. — We have seen that chlorine, bromine, iodine, and fluorine all form compounds with hydrogen which are acid. Taking these in the order of the increasing atomic weight of the halogen, we have seen that hydrofluoric acid is the most stable of all the compounds of the halogens with hydrogen. Hydrochloric acid is next, and this is followed in the order of decreasing stability by hydrobromic and hydriodic acids. Indeed, the last named substance is quite unstable.

If we turn to the compounds with oxygen and hydrogen, we find the order exactly reversed. Fluorine forms no known compound with oxygen. Chlorine forms very unstable compounds with hydrogen and oxygen, bromine still more stable compounds, while iodine forms fairly stable substances when combined with oxygen and hydrogen.

If we compare the strengths of the acids formed by the union of hydrogen with the several halogens, we would find that they were all acids, but to a very different extent. The method of determining the relative strengths of acids is to determine the relative number of hydrogen ions in their solutions, since acidity is due entirely to hydrogen ions. To determine the relative number of hydrogen ions is the same as to determine the degree of dissociation of the several substances. The dissociation of a compound is most readily determined, as we have seen, by measuring the conductivity of its solutions, and also the conductivity of its completely dissociated solution. The molecular conductivity at any dilution is known as μ_v, the molecular conductivity at complete dissociation, μ_∞. The dissociation α is the ratio between these two quantities. The molecular conductivities of a number of solutions of the compounds of the halogens with hydrogen are given below. The dilutions in the four

cases are the same, being the number of litres of the solution which contain a gram-molecular weight of the electrolyte: —

Dilution v	HCl $\mu_v(25°)$	HBr $\mu_v(25°)$	HI $\mu_v(25°)$	HF μ_v
4	343	354	353	27.8
32	369	373	372	55.8
128	376	380	380	98.2
256	378	380	380	129
μ_∞	378	380	381	380

The dissociations in each case are calculated by dividing the molecular conductivities at any given dilution by the maximum molecular conductivity of the substance.

Dilution	HCl a	HBr a	HI a	HF a
4	90.8%	93.2%	92.7%	7.3%
32	97.6	98.2	97.6	14.7
128	99.5	100.0	99.7	26.0
256	100.0	100.0	99.7	34.0

While the strengths of hydrochloric, hydrobromic, and hydriodic acids are almost exactly the same at all dilutions, that of hydrofluoric acid is very much less. Indeed, at the greater concentrations hydrofluoric acid is less than one-tenth as strong as the other halogen acids. This is one of many examples of physical chemistry correcting erroneous conceptions in inorganic chemistry.

CHAPTER XII

SULPHUR (At. Wt. = 32.06)

Occurrence and Purification. — Sulphur occurs in great abundance in nature in the free condition. This is especially true in volcanic regions such as those of Italy, Sicily, Iceland, China, etc. A volcanic region in which the deposition of sulphur is still going on is known as a *solfatara.* Sulphur also occurs in combination with a number of other elements. In combination with oxygen as sulphur dioxide, SO_2, it escapes in certain volcanic regions. Combined with hydrogen as hydrogen sulphide, H_2S, it also issues from the earth in the neighborhood of certain volcanoes. It also exists in combination with a number of metals as sulphides. We have zinc sulphide or *zinc blende,* ZnS, lead sulphide or *galena,* PbS, iron sulphide or *pyrites,* FeS_2, mercury sulphide or *cinnabar,* HgS, antimony sulphide or *stibnite,* Sb_2S_3, and copper iron sulphide or *copper pyrites,* $Cu_2Fe_2S_4$.

The sulphur which occurs in the free condition in nature does not all escape from the interior of the earth in the form of sulphur, but is deposited as the result of the action of one sulphur compound on another, or of oxygen on hydrogen sulphide: —

$$2\,H_2S + O_2 = 2\,H_2O + 2\,S,$$
$$SO_2 + 2\,H_2S = 2\,H_2O + 3\,S.$$

In this last reaction sulphur dioxide, which generally takes up oxygen and is, therefore, a reducing agent, gives up oxygen and is an oxidizing agent.

Sulphur as it occurs in nature contains more or less impurities which are generally non-volatile. The sulphur is freed from these by fusion. The first more or less crude product of molten sulphur is known as *crude brimstone.* The crude brimstone is then redistilled and either condensed in a state of fine division as *flowers of sulphur,* or the molten mass poured into moulds as *roll* or *stick sulphur.*

Chemical Properties of Sulphur. — Sulphur at ordinary temperatures is comparatively inert. Indeed, at elevated temperatures it is

less active chemically than members of the halogen group at ordinary temperatures. When heated in the presence of the air sulphur combines with oxygen, forming sulphur dioxide: —

$$S + O_2 = SO_2.$$

Sulphur, however, combines with many of the elements, forming well-defined compounds. The compounds with the acid-forming elements, such as those which we have already studied, are, in general, much less stable than the compounds of sulphur with the metals. The latter class of compounds, known as the *sulphides*, have characteristic properties which are very useful, as we shall learn, in qualitative analysis.

Physical Properties of Sulphur. — Sulphur is a yellowish solid at all ordinary temperatures, melting at 118° and boiling at 448°.4. The solid sulphur is known in two forms. If allowed to crystallize from a solution of carbon disulphide, and as found in nature, it crystallizes in the orthorhombic system; the characteristic of this system being that the three crystallographic axes are all at right angles and all of unequal length.

If, on the other hand, ordinary flowers of sulphur, roll sulphur, or orthorhombic sulphur is melted and allowed to cool slowly in a hessian crucible, we obtain the sulphur in the form of needles which do not belong at all to the orthorhombic system, but to a crystallographic system having a much lower order of symmetry — the monoclinic system. The characteristic of this system is that the three crystallographic axes are all of unequal lengths, and one of them makes an oblique angle with the other two.

Substances which can crystallize in several systems are known as *polymorphous;* when they crystallize in two systems, as *dimorphous.* Sulphur is, therefore, *dimorphous.* Below 95°.6 orthorhombic sulphur is the stable phase, while from 95°.6 to 131° monoclinic sulphur is the stable phase. This point 95°.6, at which the transformation from one solid phase to the other solid phase takes place, is known as the *transition point.* Substances which like sulphur exist in two phases of the same state of aggregation, and the two phases can be reciprocally transformed into one another by changing the temperature, are known as *enantiotropic.* Where only one form is stable under conditions which can be realized and, consequently, the unstable form can be transformed into the stable but not *vice versa,* we have what is known as *monotropism.*

In addition to the above two solid modifications of sulphur, we have solid, amorphous sulphur, exemplified by flowers of sulphur,

milk of sulphur, etc., which are insoluble in carbon disulphide and, therefore, differ from crystallized sulphur. The differences between the various solid phases of sulphur are far more deep-seated, as we would expect, than mere external form. Take the two crystalline modifications. They are obviously analogous to oxygen and ozone, the former being, however, enantiotropic, the latter monotropic, but this difference is not fundamental, simply depending upon whether the transformation point is below the melting-point.

In the case of oxygen and ozone we have seen that the fundamental and important difference is in the amount of intrinsic energy present in the molecules of the two substances. We would naturally ask whether any such difference exists between orthorhombic and monoclinic sulphur. This can be answered very simply in the case of sulphur, indeed more simply and directly than with oxygen and ozone. It is only necessary to burn equal quantities of the two modifications of sulphur in oxygen and measure the amounts of heat liberated. The products being the same in both cases — sulphur dioxide — any difference in the heats of combustion is the expression in thermal units of the difference between the intrinsic energy in orthorhombic and monoclinic sulphur.

A considerable difference was found in the amounts of heat liberated in the two cases. Thirty-two grams or a gram-atomic weight of orthorombic sulphur when burned to sulphur dioxide liberate 71,000 calories of heat. An equal weight of monoclinic sulphur burned to sulphur dioxide sets free 73,300 calories of heat. The difference, 2300 calories, is the thermal equivalent of the difference in the intrinsic energy of the two modifications.

The relations are just what we would expect from our study of oxygen and ozone. Oxygen is the more stable form under ordinary conditions, and contains the smaller amount of intrinsic energy. So, also, orthorhombic sulphur is the more stable form under ordinary conditions and contains less intrinsic energy than monoclinic.

Sulphur, as has been stated, melts at 118°. It first passes over into a thin, light-yellow liquid, which, on further rise in temperature, passes through a remarkable series of transformations. When heated to 160° the yellow liquid passes over into a reddish-brown, viscous mass, which becomes deeper brown in color and more viscous as the temperature is raised to 250°. If the temperature is still further raised until 400° is reached, the viscous mass becomes a yellow liquid again, which boils at 448°.4. When the boiling sulphur is allowed to cool, it passes through these same changes again, but in reverse order.

The vapor of sulphur when formed at its boiling temperature is reddish-brown, but this becomes much lighter in color as the temperature is raised.

Vapor-density of Sulphur.—The vapor-density of sulphur has attracted much attention, since it varies so greatly with the temperature. If sulphur is boiled under diminished pressure, so that the temperature is quite low, its vapor-density corresponds to the molecular weight 256. Since the atomic weight of sulphur is 32, the molecule of the vapor under these conditions consists of eight atoms — S_8. If sulphur is boiled under ordinary atmospheric pressure, the vapor-density corresponds to a molecular weight of 192, which means that the molecules are composed of six atoms each — S_6. If the vapor of sulphur is heated to 800° its vapor-density corresponds to a molecular weight of 70, while if the vapor is heated to 1100°, its density shows a molecular weight of 64. This corresponds to the molecule S_2.

As the temperature rises the complex molecules of sulphur break down into simpler molecules, and when a temperature of 1100° is reached, practically all of the more complex molecules have broken down into molecules containing two atoms each.

The further question arises, Do the molecules S_8 break down in stages or do they decompose at once into molecules of S_2? This has recently been answered satisfactorily by methods which it would lead us too far to discuss here. The molecules of S_8 do not first break down into molecules of S_6, S_4, etc., but decompose at once into molecules of S_2 in the following sense: —

$$S_8 = 4\,S_2.$$

The opposite opinion was held for a time, but is undoubtedly erroneous.

The Temperature-pressure Diagram of Sulphur.—If we plot the temperature-pressure diagram of sulphur as we did that of water, it would have the following form (Fig. 27): —

The diagram is considerably more complex than the diagram for water, where only three phases were present; yet the principles involved are exactly the same; and if we understood the diagram for water, this should offer no serious difficulty.

Beginning with the conditions of equilibrium between orthorhombic sulphur and sulphur vapor, these are represented by the curve *PB*. The curve PP_1 is the vapor-pressure curve of monoclinic sulphur, while P_1C is the vapor-pressure curve of liquid sulphur. The point *P* is the transition point of orthorhombic and monoclinic sul-

phur. The curve PP_{11} represents the conditions of equilibrium between orthorhombic and monoclinic sulphur, and any point on this curve is therefore a transition point. The curve P_1P_{11} represents equilibrium between monoclinic and liquid sulphur, and is therefore the curve of the melting-point of monoclinic sulphur. Just as the curve (PP_{11}) of the transition point of orthorhombic and monoclinic sulphur slopes to the right as it rises, showing an increase in temperature with increase in pressure, so the curve of the

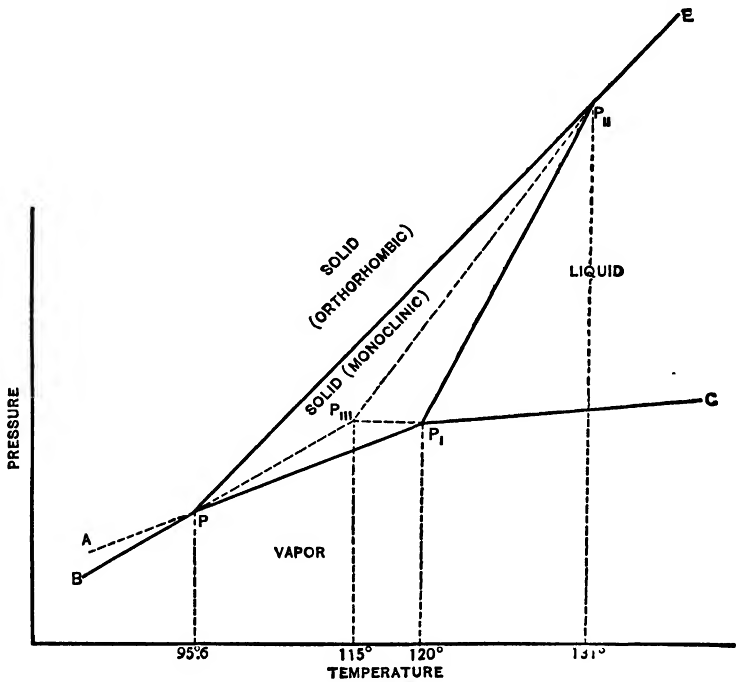


Fig. 27.

melting-point of monoclinic sulphur (P_1P_{11}) slopes to the right as it rises. This is but one of many analogies between transition points and melting-points. These two curves, however, meet at the point P_{11}, which corresponds to a temperature of 131°. The curve $P_{11}E$ is the curve of equilibrium between orthorhombic and liquid sulphur, *i.e.* the curve of the melting-point of orthorhombic sulphur with increase in pressure, monoclinic sulphur being incapable of existence beyond 131°, no matter how high the pressure.

Let us turn now to the dotted curves. PA represents the vapor-pressure of metastable monoclinic sulphur. This is greater below

the transition point, as we would expect, than the vapor-pressure of the stable orthorhombic phase. Above the transition point orthorhombic sulphur is the metastable phase, and it has in this region a higher vapor-pressure than the stable monoclinic phase. This is represented by the curve PP_{111}, the prolongation of PB. If now we prolong the curve, P_1C representing equilibrium between liquid sulphur and its vapor until it meets the prolongation of PB, it will do so at P_{111}. If now we join P_{111} and P_{11}, the curve will represent the equilibrium between orthorhombic sulphur and liquid sulphur, *i.e.* the melting-point of orthorhombic sulphur, and the effect of pressure as increasing the temperature at which this phase will melt.

We have now examined all the curves in the diagram. Let us see what kinds of systems they represent. The point P represents equilibrium between the three phases orthorhombic, monoclinic, and vapor, and is, therefore, a triple point. Similarly, P_1 represents equilibrium between monoclinic, vapor, and liquid; P_{11}, between orthorhombic, monoclinic, and liquid; and P_{111} (in the metastable region), between orthorhombic, liquid, and vapor; and these are all triple points. We have, then, four triple points, and since there is one component and three phases the systems are nonvariant.

Take the curves. PB represents equilibrium between orthorhombic and vapor, PP_1 between monoclinic and vapor, P_1C between liquid and vapor, P_1P_{11} between monoclinic and liquid, $P_{11}P$ between orthorhombic and monoclinic.

Take the dotted curves representing equilibria in metastable regions. PA is the curve of equilibrium between monoclinic and vapor, PP_{111} between orthorhombic and vapor, P_1P_{111} between liquid and vapor, and $P_{11}P_{111}$ between orthorhombic and liquid.

These systems represent conditions of equilibria between two phases, and since the number of components is one they are monovariant systems.

Take finally the areas. Within BPP_1C sulphur is stable only in the form of vapor, within $CP_1P_{11}E$ the liquid is the stable form, within $EP_{11}PB$ the orthorhombic is the stable phase, and within PP_1P_{11} the monoclinic is the stable form. These areas each represent one stable phase of the substance, and since there is only one component these systems are divariant.

So much for the conditions of equilibria where there is one component and four phases.

Compounds of Sulphur with Hydrogen. — Sulphur forms one very important compound with hydrogen — hydrogen sulphide, H_2S, and one which is far less important — hydrogen persulphide, H_2S_2.

Hydrogen Sulphide, H_2S. — This compound occurs in nature in the free condition, as we have seen. It escapes from fissures in certain localities and is dissolved in certain waters, producing *sulphur water.* Hydrogen sulphide is formed by the direct union of hydrogen and sulphur. When hydrogen and sulphur vapor are heated together, especially in the presence of porous porcelain, they combine in part, forming hydrogen sulphide. If nascent hydrogen is brought into contact with sulphur, there is a certain amount of hydrogen sulphide formed.

By far the best method of preparing hydrogen sulphide, and the one which is always employed, is to treat certain sulphides with an acid. The sulphide which it is most convenient and economical to use is ferrous sulphide, FeS. When this is treated with sulphuric or hydrochloric acid the following reaction takes place: —

$$FeS + H_2SO_4 = FeSO_4 + H_2S,$$

$$FeS + 2\,HCl = FeCl_2 + H_2S.$$

Chemical Properties of Hydrogen Sulphide. — Hydrogen sulphide is acted upon by certain metals at ordinary temperatures. Thus, silver and lead decompose it, combining with the sulphur and liberating the hydrogen.

The oxides of certain metals also react with hydrogen sulphide, forming the sulphide of the metal and water.

By far the most important chemical application of hydrogen sulphide is in connection with its action on the soluble salts of the heavy metals. Take as an example its action on solutions of silver nitrate: —

$$2\,AgNO_3 + H_2S = Ag_2S + 2\,HNO_3.$$

In such cases we have the sulphide of the metal precipitated with its characteristic properties.

It is generally true that when hydrogen sulphide is passed into solutions of salts of the heavy metals, the sulphide of the metal is precipitated. If this does not take place otherwise, it is effected by making the solution slightly alkaline.

The sulphides of certain metals resemble one another with respect to a given property. This enables us to separate the metals into groups by means of hydrogen sulphide. The sulphides of certain metals are soluble in water. Thus, the sulphides of sodium, potassium, ammonium, cæsium, lithium, rubidium, calcium, barium, strontium, magnesium dissolve readily in water, and these elements as a

group can be separated from all other elements. Other means must be employed to separate the individual members of this group from one another.

There is another group of elements whose sulphides dissolve in dilute acids. These include among the more common elements zinc, manganese, uranium, iron, cobalt, nickel.

These can be precipitated as a group, not by hydrogen sulphide, since this would necessitate the formation of free acid and the consequent solution of the sulphide, but by a soluble sulphide. The sulphide employed is ammonium sulphide, and this group of elements is known as the ammonium sulphide group. If we add ammonium sulphide to a solution containing salts of all the above elements, they would all be precipitated together.

In order to separate the several members of the group from one another, individual differences in one property or another of the sulphides must be utilized. The reaction expressing the precipitation of a sulphide by means of ammonium sulphide is —

$$ZnCl_2 + (NH_4)_2S = ZnS + 2\,NH_4Cl.$$

It is obvious that there is no acid set free in this reaction.

There remains a group of elements whose sulphides are not soluble in cold, dilute acids. These include arsenic, antimony, tin, platinum, gold, mercury, cadmium, copper, silver, lead, and bismuth. Salts of these metals are readily precipitated by hydrogen sulphide, since the acid set free does not dissolve the sulphide when formed. Thus: —

$$CdCl_2 + H_2S = CdS + 2\,HCl,$$

$$PtCl_4 + 2\,H_2S = PtS_2 + 4\,HCl,$$

$$CuSO_4 + H_2S = CuS + H_2SO_4.$$

This group of elements is known as the hydrogen sulphide group. Here again individual differences between the sulphides are utilized to separate the several members. Thus, the sulphides of the first five elements are soluble in yellow ammonium sulphide, and they are thus separated from the remaining sulphides.

Hydrogen sulphide is easily oxidized in the sense of the following equation: —

$$2\,H_2S + O_2 = 2\,H_2O + 2\,S.$$

When hydrogen sulphide in water is exposed to the air, the above reaction takes place and the sulphur is precipitated as a white

powder. Because of the ease with which hydrogen sulphide reacts with oxygen it is a good reducing agent.

Where hydrogen sulphide is passed through a tube heated to redness it decomposes in part into hydrogen and sulphur. This is very surprising when we consider that hydrogen sulphide is formed by the direct union of hydrogen and sulphur when the two are heated together. These statements seem directly contradictory. This brings us to consider a new phase of chemical reactions which we have thus far not taken up at any length.

Reversible Chemical Reactions. —We have regarded chemical reactions thus far as taking place only in one direction. Two substances, *A* and *B*, unite and form the compound *AB*, and we have written the equation expressing the reaction in the following manner: —

$$A + B = AB.$$

This regards the compound *AB* as the static or unchanging condition into which the elements *A* and *B* have passed when they combine.

This is frequently not the whole truth. The compound *AB* often undergoes decomposition at the same time that it is being formed, giving again the elements *A* and *B*. This reaction would be represented as follows: —

$$AB = A + B.$$

The reaction which took place originally between the elements *A* and *B* is exactly reversed in the second stage. Such reactions, of which there is an unlimited number, are known as *reversible reactions*. Indeed, some are of the opinion that all chemical reactions are reversible, the original reaction in some cases proceeding, however, very rapidly, while the reverse reaction proceeds very slowly. This gives us the key to the formation of a certain amount of the substance *AB* from the elements *A* and *B* when the reaction is reversible. At first we have only the elements *A* and *B*. These begin to combine and form the compound *AB* with a certain velocity which is at first very considerable, but which becomes gradually slower and slower as the amounts of *A* and *B* become less and less. At first there is none of the compound *AB* present, only the uncombined elements. When *AB* begins to form, the reverse reaction resulting in its decomposition into *A* and *B* begins, but at first has very small velocity. As the amount of the compound *AB* increases, the velocity with which it is decomposed also increases. The result is that the velocity of the original reaction is becoming less and less,

while the velocity of the reversed reaction is becoming greater and greater. After a time the two velocities become equal and we have then the condition described as *equilibrium.*

When equilibrium is reached, it does not mean that the original reaction has ceased or that the reversed reaction has ceased, but that the two are taking place with the same velocity, just as much of the compound *AB* decomposing in a given time as is formed in a given time. This is the same as to say that the condition of equilibrium is not a static condition as was for a long time supposed, but is a *dynamic condition.* The importance of the recognition of this fact is very great indeed. It underlies the entire chapter of chemical dynamics and equilibrium, which is one of the most important in modern physical chemistry.

Let us apply this conception to the reaction under consideration. Hydrogen and sulphur combine forming hydrogen sulphide, with a velocity which becomes less as the quantity of the elements present decreases. Hydrogen sulphide decomposes into hydrogen and sulphur, with a velocity which becomes greater as the amount of hydrogen sulphide present increases; after a time just as much hydrogen sulphide being decomposed in a given unit of time as is formed in the same time. Equilibrium between the two reactions is then established.

When equilibrium is established we have the maximum amount of hydrogen sulphide formed, which, under the conditions ever could be formed. This is usually referred to as the *yield of the reaction.*

All chemical reactions in which the yield is less than one hundred per cent are reversible, and since this theoretical yield is probably never quite fully realized, all reactions are probably strictly speaking reversible.

In some cases, however, the combination is so nearly complete that we must regard the velocity in one direction as infinitely great with respect to the velocity in the reverse direction. In such cases we would have, when equilibrium was reached, nearly all of *A* and *B* combined to form the compound *AB*, while a very slight amount of *AB* was decomposed into *A* and *B*. This is the condition which obtains in most reactions where a solid is precipitated. The solid is formed with a velocity which is usually far too great to measure, and the reaction proceeds nearly to the end before equilibrium between the two opposite reactions is established.

Only such reactions can be used in quantitative analysis which depend upon the reaction in one direction being practically complete.

Acid Sulphides. — Hydrogen sulphide, as we have seen, has the composition H_2S, and forms salts with univalent elements having the composition M_2S, M representing any univalent element. If M represents a bivalent element, the salt has the composition MS.

Hydrogen sulphide can also form a different class of salts in which one of the hydrogen atoms is still present. With univalent elements these would have the general composition MHS, with bivalent elements $M(HS)_2$. The acid in these salts is *monobasic* — one molecule of the acid, as we usually express it, combining with one ion of a univalent element. We have a number of examples of these *hydrosulphides* or *acid sulphides* as they are called. Ammonia forms the hydrosulphide very readily when hydrogen sulphide is conducted into aqueous ammonia: —

$$NH_3 + H_2S = NH_4HS.$$

Indeed, this is the compound which is formed when aqueous ammonia is saturated with hydrogen sulphide. In order to form the normal sulphide, an equal quantity of ammonia must be added to the hydrosulphide: —

$$NH_4HS + NH_3 = (NH_4)_2S.$$

Many hydrosulphides are known, such as NaHS and KHS. Indeed, those metals in general, whose sulphides are soluble in water, form hydrosulphides.

Dissociation of Hydrogen Sulphide. — The hydrosulphides or acid sulphides are, as we have seen, salts of a monobasic acid. The sulphides, on the other hand, are salts of a *dibasic acid, i.e.* one which combines with two univalent ions. How can we explain these facts on the basis of the dissociation theory?

There are two different ways in which hydrogen sulphide can dissociate. These are the following: —

$$H_2S = \overset{+}{H}, \overset{-}{HS}, \tag{1}$$

$$H_2S = \overset{+}{H}, \overset{+}{H}, \overset{=}{S}. \tag{2}$$

When the compound dissociates as in equation (2), it is obviously dibasic; when the dissociation takes place as in equation (1), it is monobasic. This is the general method by which dibasic acids dis-

sociate. Take as a general example H_2A, in which A is the anion of the dibasic acid. This dissociates first into $\overset{+}{H}$ and $H\overset{-}{A}$: —

$$H_2A = \overset{+}{H}, H\overset{-}{A}.$$

The anion $H\overset{-}{A}$ contains the anion proper combined with a hydrogen atom. If the dilution of the solution is still further increased, this breaks down into $\overset{+}{H}$, $\overset{=}{A}$: —

$$H\overset{-}{A} = \overset{+}{H}, \overset{=}{A}.$$

When the dissociation has taken place in the sense of (2), the acid is completely dissociated, and we have a dibasic acid.

The amount of the dissociation in terms of (1) or (2) at any given dilution is determined solely by the nature of the acid. If the acid is very strong it begins to dissociate in terms of (2) before any very great dilution is reached, while if the acid is weak it may require very high dilution to effect any appreciable amount of dissociation in the sense of the second equation.

The salts of acids such as we have been considering dissociate very much like the acids themselves. The hydrosulphide or acid sulphide of sodium, NaHS, dissociates thus: —

$$NaHS = \overset{+}{Na}, H\overset{-}{S}.$$

The anion $H\overset{-}{S}$, being the anion of a weak acid, dissociates slightly into $\overset{+}{H}$, $\overset{=}{S}$, but only slightly. A *few hydrogen ions* are thus formed in the solution of sodium hydrosulphide or acid sulphide, and these give the characteristic acid reaction of this salt with indicators. The acid reaction is, however, weak, since there are relatively only a few hydrogen ions present in the solution. If substances like hydrogen sulphide dissociate as monobasic acids yielding only one hydrogen ion, why do they react like dibasic acids when treated with a solution of a strong base like sodium hydroxide? The answer to this apparently difficult question is very simple. The sodium hydroxide reacts with all the dissociated portion of the hydrogen sulphide thus: —

$$H\overset{-}{S}, \overset{+}{H} + \overset{-}{O}H, \overset{+}{Na} = H_2O + \overset{+}{Na}, H\overset{-}{S}.$$

All the hydrogen ions originally present are, therefore, combined with the hydroxyl anion to form water and removed from the field of action. As soon as this has taken place, we have the remaining undissociated portion of the acid under the same conditions as the original acid — in the presence of water in which there are no hydro-

gen ions. The dissociation will then proceed until all the molecules have been broken down in the sense of (1). If more sodium hydroxide is now added, we would have in the solution an excess of hydroxyl ions, and these will cause the anion $\overset{-}{HS}$ to dissociate to a much greater extent than it would do in the presence of water alone; since as fast as hydrogen ions are formed they combine with hydroxyl ions from the sodium hydroxide, form water and are removed from the field of action. There is thus no accumulation of hydrogen ions as in the case of water alone, and the dissociation proceeds until all the ions $\overset{-}{HS}$ have dissociated into $\overset{+}{H}, \overset{=}{S}$. Hydrogen sulphide therefore acts as a dibasic acid towards a strong base.

Physical Properties of Hydrogen Sulphide. — Hydrogen sulphide is a colorless gas with an extremely disagreeable odor, suggesting decomposing organic matter. When taken into the lungs in any great quantity, it is quite poisonous. For this reason and on account of its disgusting odor it should never be allowed to escape into the air of a laboratory. Since it is so frequently used in connection with qualitative analysis, a separate room is attached to every well-equipped chemical laboratory in which the gas is generated and used. This is known as the "sulphuretted hydrogen" room.

Hydrogen sulphide dissolves in water to the extent of from $2\frac{1}{2}$ to 3 volumes of the gas in one volume of water. Even at such concentrations the law of Henry holds — the amount of gas dissolved is proportional to the pressure to which the gas is subjected. The law of Henry, in general, holds better the more dilute the solution, *i.e.* the less the solubility of the gas.

A solution of hydrogen sulphide in water soon becomes cloudy, due to the deposition of sulphur, the hydrogen sulphide being oxidized, as we have seen, by the oxygen of the air, yielding water and sulphur.

When hydrogen sulphide is subjected to a pressure of fifteen atmospheres at ordinary temperatures, it passes over into a colorless liquid having a specific gravity of 0.9. When cooled to $-85°$, it solidifies. Liquid hydrogen sulphide is somewhat explosive.

Hydrogen Persulphides. — There are a number of compounds of sulphur with potassium which contain much more sulphur than potassium sulphide — K_2S. These are K_2S_2, K_2S_3, K_2S_4, and K_2S_5. These are formed by the union of potassium sulphide with sulphur. When an ordinary solution of ammonium sulphide is allowed to stand in contact with the air for a time, a part of it is oxidized with liberation of sulphur, which then combines with the ammonium sul-

phide forming polysulphides of ammonia. This is shown by the change from the colorless ammonium sulphide to the deep-yellow polysulphides of ammonia.

When any of these polysulphides is treated with an acid, it gives off hydrogen sulphide, and sulphur is set free. When, however, the process is reversed and the solution of the polysulphide added to the acid, no hydrogen sulphide is formed, but a yellow, oily liquid separates. The composition of this liquid probably depends on the particular polysulphide which is present. It is probably the acid corresponding to the polysulphide in question. The fact is that we almost always have a mixture of a number of these polysulphides, and when we pour such a mixture into an acid, the resulting oil probably contains a number of hydrogen persulphides, ranging in composition from H_2S_2 to H_2S_5.

This whole question of the composition of the hydrogen persulphides is, however, still an open one.

COMPOUNDS OF SULPHUR WITH OXYGEN AND HYDROGEN

Sulphur Dioxide, SO_2. — The simplest compound of sulphur and oxygen is sulphur dioxide, having the composition SO_2. It is formed by the direct combination of the two elements when sulphur is burned in oxygen: —

$$S + O_2 = SO_2.$$

A more convenient method of preparing sulphur dioxide is by the action of strong acids on sulphites, or acid sulphites. Normal potassium sulphite has the composition K_2SO_3. When this is treated with sulphuric acid the following reaction takes place: —

$$K_2SO_3 + H_2SO_4 = K_2SO_4 + H_2O + SO_2.$$

The acid sulphite has the composition $KHSO_3$. When this is treated with sulphuric acid we have: —

$$2\,KHSO_3 + H_2SO_4 = K_2SO_4 + 2\,H_2O + 2\,SO_2.$$

Another very convenient method for preparing sulphur dioxide is by the action of sulphuric acid on metallic copper. The reaction may be regarded as taking place as follows: —

$$Cu + H_2SO_4 = CuSO_4 + H_2.$$

The nascent hydrogen then reduces the sulphuric acid: —

$$H_2SO_4 + H_2 = 2\,H_2O + SO_2.$$

Its most characteristic chemical properties are its oxidizing and reducing actions. Under certain conditions it gives up its oxygen, serving as an oxidizing agent; under other conditions it readily takes up oxygen, passing over into sulphur trioxide, SO_3, and is, therefore, an excellent reducing agent.

The composition of sulphur dioxide is determined by the following considerations. When sulphur is burned in oxygen the volume of the sulphur dioxide formed is just equal to the volume of the oxygen used up. From Avogadro's law there are, therefore, the same number of molecules of sulphur dioxide formed as there were molecules of oxygen used up. Each molecule of oxygen, however, contains two atoms of oxygen; therefore, each molecule of sulphur dioxide must contain two atoms of oxygen.

It is a colorless gas with very penetrating odor, and a taste which persists for an unusual time. Its odor and taste are characteristic of a burning sulphur match, with which every one is familiar. It does not obey the laws of gas-pressure, being too near its point of liquefaction. Its critical temperature is 157°, and its critical pressure is 79 atmospheres. It can, therefore, be readily liquefied. At ordinary temperatures it is liquefied if subjected to a pressure of three atmospheres. If cooled by a mixture of salt and ice it readily liquefies under atmospheric pressure. Liquid sulphur dioxide is perfectly clear and transparent, boiling at −10°. It can be readily solidified when allowed to evaporate under diminished pressure, a temperature of − 50° to − 60° being produced. Liquid sulphur dioxide is an excellent solvent for a large number of substances, and according to the recent work of the Russian, Walden, has considerable power to dissociate electrolytes into their ions. Indeed, solutions of certain salts in liquid sulphur dioxide frequently show better conductivity than solutions of the same salts at the same concentrations in water. It is readily obtained on the market in steel cylinders. Sulphur dioxide dissolves readily in water, one volume of water at ordinary temperatures dissolving about fifty volumes of the dioxide. The solution of sulphur dioxide in water has an acid reaction and is known as sulphurous acid.

Sulphurous Acid, H_2SO_3. — The acid formed when sulphur dioxide is dissolved in water yields salts having the composition M_2SO_3, where M is a univalent metal. The acid must therefore have the composition H_2SO_3, and be a dibasic acid. It can also form acid sulphites of the composition $MHSO_3$.

It has been impossible to isolate the acid H_2SO_3, since it breaks down so readily into water and sulphur dioxide.

$$H_2SO_3 = H_2O + SO_2.$$

A hydrate containing a much larger amount of water has, however, been isolated. This is a crystallized solid having the composition $H_2SO_3 . 14 H_2O$.

Sulphurous acid is much more easily oxidized than sulphur dioxide, and is, therefore, a much better reducing agent. When brought in contact with substances rich in oxygen, some of the oxygen is removed, and the sulphurous acid is converted into an acid richer in oxygen — sulphuric acid. Thus, sulphurous acid, in the presence of the beautifully violet potassium permanganate, takes oxygen away from this compound, entirely destroying its color, and being itself converted into sulphuric acid. We shall study this action more in detail under manganese. Sulphur dioxide is also an excellent bleaching agent.

Dissociation of Sulphurous Acid. — Sulphurous acid is a weak acid. Being a dibasic acid, it can dissociate in two ways: —

$$H_2SO_3 = \overset{+}{H}, H\overset{-}{S}O_3$$

is the first stage in the dissociation. Since the acid is weak, it requires very high dilution — a very large amount of water present — to effect the dissociation of the ion $H\overset{-}{S}O_3$. When the dilution is sufficient, this, however, breaks down into $\overset{+}{H}$ and $\overset{=}{S}O_3$. The second stage in the dissociation would then be represented thus: —

$$H\overset{-}{S}O_3 = \overset{+}{H}, \overset{=}{S}O_3.$$

Sulphur Trioxide, SO_3. — Sulphur trioxide, SO_3, is formed by gently heating "fuming sulphuric" acid. The latter is really a solution of sulphur trioxide in sulphuric acid, usually having approximately the composition $H_2S_2O_7$. When this is heated, it decomposes thus: —

$$H_2S_2O_7 = H_2SO_4 + SO_3.$$

It is also obtained by heating ordinary sulphuric acid in the presence of some substance which will take up water. Such a substance is the pentoxide of phosphorus, P_2O_5. The reaction which takes place is

$$H_2SO_4 + P_2O_5 = 2 HPO_3 + SO_3.$$

When sulphur dioxide and oxygen are heated together, they combine and form sulphur trioxide, but only in very small quantity. If, however, the mixture of the two gases is heated in the presence of certain substances, they combine readily, forming sulphur trioxide. Such a substance is ferric oxide, and still better, finely

divided platinum. If the two gases are passed through a tube containing platinum sponge, and the tube heated, they combine very readily. Instead of using platinum sponge, it has been found to be more economical to use asbestos covered with finely divided platinum — platinum asbestos.

This is distinctively a *catalytic reaction*, the platinum in this case does not enter at all into the reaction, and a very small amount of platinum is capable of effecting a large amount of the reaction. This method of preparing sulphur trioxide has been found to be so efficient and economical that it is rapidly supplanting all others, and in the near future will probably be used almost exclusively for preparing this substance. The sulphur dioxide obtained by roasting various sulphur ores, and especially pyrite, is mixed with air and passed over heated platinum asbestos. The sulphur trioxide is then dissolved in concentrated sulphuric acid, forming the so-called solid sulphuric acid, having the composition $H_2S_2O_7$.

Properties of Sulphur Trioxide. — Sulphur trioxide is a powerful oxidizing agent, readily giving up one of its oxygen atoms and passing over into sulphur dioxide. It has an unusual attraction for water, combining with it at once on mere contact, and even causing the hydrogen and oxygen in organic compounds to combine and form water with which it instantly combines.

Sulphur trioxide is a transparent, mobile liquid, which boils at 46°.2. It can be cooled to zero without solidifying. When further cooled it forms a white solid, which melts at 14°.8.

When kept at ordinary temperatures it undergoes polymerization, passing into a white solid composed of fine needles, having the general appearance of asbestos. This form, which is very probably a polymer of the other, is the stable modification. When it is heated it does not melt, but passes at once into vapor. When the vapor is condensed it forms the liquid first referred to.

One reason for supposing that the solid is a polymer of the liquid form, is that the latter is the stable modification at higher temperatures where polymers tend to pass into simpler forms, and is formed directly by condensing the vapor, in which form the molecule is generally the simplest possible.

Sulphur trioxide dissolves in water with a crackling sound, and with the evolution of an enormous amount of heat, forming sulphuric acid.

Sulphuric Acid, H_2SO_4. — Sulphuric acid occurs, in the free condition, in small quantity in certain waters on the surface of the earth, and in abundance in sulphates. It is prepared now very

largely by the method described above, — by the action of water on sulphur trioxide, —

$$SO_3 + H_2O = H_2SO_4,$$

the trioxide being easily formed by the direct union of sulphur dioxide and oxygen in the presence of finely divided platinum. At an earlier date a method was employed for effecting the oxidation of sulphur dioxide, which even to-day finds considerable application. This method is based upon the oxidation of sulphur dioxide in the presence of water, nitric acid, and air.

The sulphur dioxide produced by roasting sulphides, or heating sulphur in contact with an abundant supply of air, is conducted through a tower known as the *Glover tower*. This is filled with fire-brick, over which dilute sulphuric acid trickles. The gas is cooled, and, at the same time, the dilute sulphuric acid loses water and is concentrated.

Concentrated sulphuric acid, containing the oxides of nitrogen, is brought in contact with the more dilute sulphuric acid, when it sets free these oxides which now mix with the sulphur dioxide. Nitric acid is then introduced, in the form of vapor, and also water-vapor. The mixture of gases containing sulphur dioxide, nitric acid, oxides of nitrogen, and water-vapor, are conducted into a chamber lined with lead, — the so-called *leaden chamber*. In these chambers, of which there are a series, the oxidation of the sulphur dioxide to sulphur trioxide takes place, and the union of the sulphur trioxide with water, forming sulphuric acid.

In order to avoid loss of nitric acid and oxides of nitrogen, which are expensive, the sulphuric acid formed in the leaden chambers is passed through another tower, known as the *Gay-Lussac tower*. This tower contains pieces of coke over which concentrated sulphuric acid flows. The concentrated acid takes up the oxides of nitrogen. This acid is then passed into the Glover tower, where it mixes with the more dilute sulphuric acid, and gives up the oxides of nitrogen which then oxidize more sulphur dioxide to the trioxide, and the process is thus a continuous one, — a small amount of nitric acid serving to oxidize a large amount of sulphur dioxide.

The chemical reactions which take place in the manufacture of sulphuric acid by the above method, as far as they are known, are the following: —

Nitric acid acts upon sulphur dioxide in the presence of water as follows: —

$$2\,SO_2 + 2\,HNO_3 + H_2O = 2\,H_2SO_4 + N_2O_3.$$

When the sesquioxide of nitrogen, N_2O_3, reacts with water-vapor it forms nitrous acid: —

$$N_2O_3 + H_2O = 2\,HNO_2.$$

When nitrous acid reacts with sulphur dioxide in the presence of the oxygen of the air, we have —

$$2\,SO_2 + 2\,HNO_2 + O_2 = 2\,NO_2.SO_3H.$$

The compound $NO_2.SO_3H$, is known as *nitrosyl-sulphuric acid*, or *nitrosulphonic acid*. When this is treated with water the following decomposition takes place: —

$$NO_2.SO_3H + H_2O = H_2SO_4 + HNO_2.$$

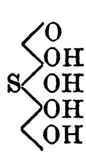
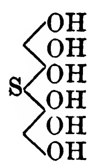
The HNO_2, or its anhydride, N_2O_3, then reacts with more sulphur dioxide and oxygen and forms again $NO_2.SO_3H$, which then decomposes with water-vapor in the sense of the last equation, and the process is continuous, the nitrous acid or sesquioxides of nitrogen being collected in the Gay-Lussac tower, as we have seen.

The acid obtained from the leaden chambers is known as "chamber acid." It contains about 65 per cent of the compound H_2SO_4. In order to further concentrate this acid it is allowed to flow through hot, shallow, lead pans, and when the acid has become sufficiently concentrated to act chemically upon the lead, it is transferred to a platinum vessel and more of the water distilled off. The acid thus obtained has a specific gravity of 1.82, and is ordinary, commercial, concentrated sulphuric acid. The acid can be still further concentrated in vessels of platinum.

Chemical Properties of Sulphuric Acid. — One of the most characteristic properties of sulphuric acid is its power to take up water and combine with it. For this reason it is an excellent drying agent, readily taking water from other substances. When we wish to dry a gas which contains water-vapor, the best method with one exception is to allow the gas to stream slowly in fine bubbles through concentrated sulphuric acid. Its power to combine with water is the key to many of the reactions which concentrated sulphuric acid can effect. When brought in contact with many organic substances, it causes the hydrogen and oxygen to combine and form water with which it itself combines. This is the explanation of the charring of wood and similar substances effected by the concentrated acid. The hydrogen and oxygen in the wood or other organic matter combine, form water which is taken up by the acid, and free carbon remains behind as a black substance.

The power of sulphuric acid to cause the elements of water to combine is the cause of a number of chemical reactions, where one of the substances contains among other things hydrogen, and the other substance oxygen and something else. The hydrogen of the one compound and the oxygen of the other combine, and the remainder of the first compound frequently combines with the remainder of the second compound, giving rise to a new substance. Sulphuric acid, thus, apparently by its contact, effects many reactions which would not take place without the presence of a dehydrating agent. Its reaction is, however, not catalytic, since it enters into the reaction in the sense that it combines with one of the products of the reaction.

Since sulphuric acid has such a remarkable power to combine with water, we would naturally ask, Does it simply mix with the water mechanically, or does it form compounds with it? Sulphuric acid combines with water, forming two compounds, $H_2SO_4.H_2O$ and $H_2SO_4.2\,H_2O$. These compounds are usually regarded as having the following formulas:—

 and 

being respectively sulphur combined with one oxygen and four hydroxyls, and with six hydroxyls — the limit if sulphur is hexivalent.

There is no satisfactory evidence that sulphuric acid can combine with a larger number of molecules of water.

Sulphuric acid has the power of driving more volatile acids out of their salts, combining with the metal of the salt. Thus, when a dry chloride or nitrate is treated with sulphuric acid, the hydrochloric or nitric acid is driven out and the sulphate of the metal is formed:—

$$2\,NaCl + H_2SO_4 = Na_2SO_4 + 2\,HCl;$$
$$2\,NaNO_3 + H_2SO_4 = Na_2SO_4 + 2\,HNO_3.$$

This might seem to argue that sulphuric acid was a stronger acid than either hydrochloric or nitric. Such, however, is not necessarily the case. Hydrochloric and nitric acids being volatile are displaced by much weaker, non-volatile acids, in accordance with the general principle that *whenever a volatile compound can be formed and escape from the field of action, it is formed.*

The true measure of the relative strengths of acids is their relative

dissociation, as we have seen; *i.e.* the relative concentrations of the hydrogen ions in their solutions. If we study the dissociation of sulphuric acid, we shall learn that it is much weaker than either hydrochloric or nitric acid.

v	μ_v (28°)	a
2	390.0	54.7%
32	490.0	68.7
1024	697.0	97.7
4096	713.0	100.0
8192	713.0	100.0

Sulphuric acid combines with most of the metals or base-forming elements, forming sulphates. In all of these compounds the sulphuric acid is bivalent, combining with two atoms of a univalent metal, with one atom of a bivalent metal, and so on. The sulphates are very stable, well-crystallized compounds. The sulphates of the heavy metals are generally only slightly soluble in water. The insolubility of its barium salt even in dilute acids furnishes us with a means of detecting sulphuric acid and determining it quantitatively. When sulphuric acid in very small quantity is added to any soluble barium salt, white, insoluble, barium sulphate — $BaSO_4$ — is precipitated.

Physical Properties of Sulphuric Acid. — Sulphuric acid, or oil of vitriol, which is the monohydrate of sulphur trioxide ($SO_3.H_2O = H_2SO_4$) is, as its name implies, a liquid. It is a thick, oily liquid with a specific gravity of 1.84. It boils at 338°, undergoing partial decomposition. When the vapor is heated to higher temperatures it breaks down into sulphur trioxide and water. When sulphuric acid is cooled below zero, it solidifies, the solid not melting until a temperature of 10°.5 is reached. When this solid is melted, it must be cooled again to zero before it will resolidify. This is evidently simply a case of an undercooled liquid, since, if a crystal of the solid is added to the liquid at zero, more of the solid will separate until a temperature of 10°.5, its true freezing-point, is reached.

Sulphuric acid dissolves readily in water with large evolution of heat and a considerable contraction in volume.

Dissociation of Sulphuric Acid. — Sulphuric acid is a typical dibasic acid, forming two well-defined classes of salts — the normal sulphates and acid sulphates. The former have the composition M_2SO_4 and the latter $MHSO_4$.

Like dibasic acids in general sulphuric acid dissociates in two stages. At first it breaks down, thus:—

$$H_2SO_4 = \overset{+}{H}, H\overset{-}{S}O_4.$$

When the dilution of the solution is increased, *i.e.* when more water is added, the ion $H\overset{-}{S}O_4$ dissociates, thus:—

$$H\overset{-}{S}O_4 = \overset{+}{H}, \overset{=}{S}O_4.$$

Sulphuric acid is a strong dibasic acid, and, therefore, the ion $H\overset{-}{S}O_4$ dissociates into $\overset{+}{H}$ and $\overset{=}{S}O_4$ before any very great dilution is reached. Sulphuric acid at a dilution of from 1000 to 2000 litres, *i.e.* in solutions containing a gram-molecular weight of the acid in one or two thousand litres, is completely dissociated into two hydrogen ions and the ion $\overset{=}{S}O_4$. This is shown by the fact that the molecular conductivity of sulphuric acid does not increase beyond these dilutions, and is sufficiently large to show that the molecule has dissociated into two hydrogen ions and not one.

The two classes of sulphates dissociate quite differently. The normal sulphates dissociate as we would expect:—

$$M_2SO_4 = \overset{+}{M}, \overset{+}{M}, \overset{=}{S}O_4;$$

the acid sulphates thus:—

$$MHSO_4 = \overset{+}{M}, H\overset{-}{S}O_4.$$

When the dilution is sufficient the ion $H\overset{-}{S}O_4$ dissociates further as follows:—

$$H\overset{-}{S}O_4 = \overset{+}{H}, \overset{=}{S}O_4.$$

A dilute solution of an acid sulphate, therefore, contains hydrogen ions and should react acid.

Such is the fact. A solution of an acid sulphate of even such strong base-forming elements as sodium and potassium, is distinctly acid. The concentration of the hydrogen ions in solutions of acid sulphates has been measured. There are methods for detecting the concentration of one kind of ions in the presence of other kinds of ions. Thus, cane sugar is inverted as we say, *i.e.* broken down into dextrose and fructrose only by hydrogen ions, and the velocity of the inversion is a function of the concentration of the hydrogen ions present. This reaction has actually been used to determine the concentration of the hydrogen ions in a solution of acid salts, where other ions are always present.

It is obvious that the conductivity method could not be used in such cases, since all kinds of ions take part in conducting the current.

Scientific and Technical Uses of Sulphuric Acid. — Sulphuric acid is used very frequently in the scientific laboratory, and far more frequently in technical processes than any other acid. In scientific operations it is used as a dehydrating agent, as a drying agent, to liberate volatile acids from their compounds, and in many other processes. In the arts it is used on every hand, and crude sulphuric acid is manufactured by the hundreds of thousands of tons annually. It is used to render normal phosphates soluble in water by converting them into acid phosphates, which can be assimilated by plants. These are the basis of most of the commercial fertilizers. It is also used in connection with the manufacture of chlorine from sodium chloride, and in the preparation of soda. When sodium chloride is treated with a molecular quantity of sulphuric acid, the following reaction takes place: —

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

The acid sulphate acts at a higher temperature upon another molecule of sodium chloride thus: —

$$NaHSO_4 + NaCl = Na_2SO_4 + HCl.$$

Sulphuric acid is at present extensively used in connection with the generation of electrical energy in *accumulators*, or *storage cells*. In such cells the electrodes are plates of lead and the electrolyte dilute sulphuric acid. When the electric current is passed through such cells, a change takes place which we shall consider under lead. If the electrodes are joined after the cell is "charged," an electric current flows in the direction opposite to that of the charging current.

Other Compounds of Sulphur with Oxygen and Hydrogen. — The two acids already considered, sulphurous and sulphuric, are the most important compounds of sulphur with oxygen and hydrogen. Several other compounds, however, are known, and these must be considered briefly. These compounds, which are all acids, are the following: —

Thiosulphuric Acid	$H_2S_2O_3$
Hydrosulphurous Acid	$H_2S_2O_4$
Pyrosulphuric Acid	$H_2S_2O_7$
Persulphuric Acid	$H_2S_2O_8$
Dithionic Acid	$H_2S_2O_6$
Trithionic Acid	$H_2S_3O_6$
Tetrathionic Acid	$H_2S_4O_6$
Pentathionic Acid	$H_2S_5O_6$
Hexathionic Acid	$H_2S_6O_6$

Thiosulphuric Acid, $H_2S_2O_3$. — Salts of this acid are formed by boiling sulphites with sulphur, —

$$Na_2SO_3 + S = Na_2S_2O_3,$$

or by the action of iodine on a mixture of sulphide and sulphite.

$$Na_2S + Na_2SO_3 + 2\,I = 2\,NaI + Na_2S_2O_3.$$

The free acid is very unstable, existing only in dilute, aqueous solution, and under these conditions for only a short time.

The sodium salt, which should be called sodium thiosulphate, but which is frequently called hyposulphite, or in the arts simply "hypo," is important in connection with photography. Its solution dissolves the halogen salts of silver, and it is, therefore, used for "fixing" photographs.

Sodium thiosulphate is easily oxidized to the sulphate, and is, therefore, a good reducing agent. It is consequently used to remove the last traces of chlorine in bleaching, and has come to be known as *antichlor.*

When the thiosulphates are treated with a dilute solution of an acid, the following reaction takes place: —

$$Na_2S_2O_3 + 2\,HCl = 2\,NaCl + H_2O + SO_2 + S.$$

Hydrosulphurous Acid, $H_2S_2O_4$. — The sodium salt has the composition $Na_2S_2O_4 \cdot 2\,H_2O$. Therefore the acid is $H_2S_2O_4$. The acid and its salts are strong reducing agents.

Pyrosulphuric Acid or Disulphuric Acid, $H_2S_2O_7$. — A salt of this acid can be obtained by heating an acid salt of sulphuric acid: —

$$2\,KHSO_4 = H_2O + K_2S_2O_7.$$

The free acid is prepared either by dissolving sulphur trioxide in sulphuric acid, —

$$H_2SO_4 + SO_3 = H_2S_2O_7,$$

or by heating ferrous sulphate in the presence of water-vapor, —

$$4\,FeSO_4 + H_2O = 2\,SO_2 + 2\,Fe_2O_3 + H_2S_2O_7.$$

This is known as *Nordhausen sulphuric acid,* or fuming sulphuric acid.

Persulphuric Acid, $H_2S_2O_8$. — This acid is obviously the hydrate of sulphur septoxide, S_2O_7.

$$S_2O_7 + H_2O = H_2S_2O_8.$$

Its salts are prepared by the electrolysis of cold, concentrated solutions of sulphates.

Most of the salts of persulphuric acid are easily soluble in water, including even the barium salt. These are, as would be expected, excellent oxidizing agents. Potassium persulphate dissolved in sulphuric acid has been shown to have remarkable oxidizing properties, and is known from its discoverer as *Caro's liquid*. This liquid has come very much to the front in the last few years, and has been the basis of a number of important investigations in the laboratory of the German chemist, Baeyer. According to him it probably contains a substance, H_2SO_5, which we may call *permonosulphuric acid*.

Polythionic Acids. — These include di-, tri-, tetra-, penta-, and hexathionic acids, having the respective compositions, $H_2S_2O_6$, $H_2S_3O_6$, $H_2S_4O_6$, $H_2S_5O_6$, and $H_2S_6O_6$.

These compounds are formed in general by the action of iodine in different quantities on sulphites or thiosulphates. The free acids are in general unstable and easily decomposed.

COMPOUNDS OF SULPHUR WITH THE HALOGENS AND OXYGEN

Compounds of Sulphur with Chlorine. — Sulphur combines with chlorine, probably forming several compounds. One of these is a fairly stable substance, having the composition S_2Cl_2, and is called *sulphur monochloride*. This compound is formed when dry chlorine gas is conducted over molten sulphur. It is a reddish-brown liquid boiling at 137°. Its vapor-density shows that it has the double formula S_2Cl_2, and not the single. Sulphur monochloride readily dissolves chlorine at low temperatures, probably forming the compounds SCl_2 — sulphur dichloride, and SCl_4 — sulphur tetrachloride. These compounds are, however, still somewhat in doubt.

Sulphur combines also with bromine, iodine, and fluorine.

Compounds of Sulphur with Chlorine and Oxygen. — There are two well-known compounds of sulphur with oxygen and chlorine. When sulphur dioxide is treated with phosphorus pentachloride, the compound $SOCl_2$ is formed, boiling at 78°. This is known as *thionyl chloride*. When thionyl chloride is treated with water the following reaction takes place: —

$$SOCl_2 + 2\,H_2O = H_2SO_3 + 2\,HCl.$$

Since sulphurous acid is formed from thionyl chloride by the action of water upon it, it is sometimes known as the chloride of sulphurous acid.

When chlorine gas is allowed to act on sulphur dioxide, another compound of sulphur with chlorine and oxygen is formed: —

$$SO_2 + Cl_2 = SO_2Cl_2.$$

This is known as *sulphuryl chloride*, and is a liquid, boiling at 69°. When treated with an excess of water, sulphuryl chloride breaks down into hydrochloric and sulphuric acids: —

$$SO_2Cl_2 + 2\ H_2O = H_2SO_4 + 2\ HCl.$$

When one molecule of sulphuryl chloride is treated with one molecule of water, the following reaction takes place: —

$$SO_2Cl_2 + H_2O = HCl + SO_2Cl(OH).$$

The compound, SO_2ClOH, *chlorsulphuric acid*, is also formed by the direct union of hydrochloric acid and sulphur trioxide: —

$$HCl + SO_3 = SO_2Cl(OH).$$

When treated with water it decomposes into hydrochloric acid and sulphuric acid: —

$$SO_2Cl(OH) + H_2O = H_2SO_4 + HCl.$$

There is another compound of chlorine, oxygen, and sulphur known. It is obtained by dehydrating chlorsulphuric acid by phosphorus pentoxide: —

$$2\ SO_2Cl(OH) = H_2O + S_2O_5Cl_2.$$

It is known as *pyrosulphuryl chloride.*

CHAPTER XIII

SELENIUM AND TELLURIUM

There are two elements occurring in comparatively small quantity, which closely resemble sulphur in their properties. These are selenium and tellurium. A few of their compounds will be considered very briefly.

SELENIUM (At. Wt. = 79.2)

Selenium was discovered in 1817 by the Swedish chemist Berzelius. It occurs in the same general associations as sulphur, and frequently along with sulphur. It occurs in combination with silver and copper as definite minerals. It is frequently found in the dust of flues where sulphides are roasted, or in the chambers in the manufacture of sulphuric acid. Like sulphur, selenium occurs in more than one modification. A number of allotropic forms have been described. If amorphous selenium is dissolved in carbon disulphide and the solution evaporated to crystallization, red crystals separate, which melt at 175.° Selenium in the amorphous condition melts at 217°. When kept at an elevated temperature, say 125° to 140°, for a considerable time, the amorphous variety becomes crystalline, gray in color, and has somewhat of a metallic lustre. In this condition, known as *metallic selenium*, it has very different properties from ordinary selenium. It is insoluble in carbon disulphide, and thus resembles flowers of sulphur. It differs from all the varieties of sulphur in being able to conduct the electric current. The amount of its conductivity depends on the intensity of the light to which it is exposed, varying considerably in a very short time with the degree of the illumination to which the selenium is exposed. It has been proposed to utilize this property of metallic selenium in transmitting sound by means of light, and an instrument known as the *photophone* has been constructed for this purpose, but has never met with any great success.

Selenium boils at 650°, the vapor-density decreasing with rise in temperature. When a temperature of 1400° is reached the vapor-density becomes constant, and corresponds to a molecular weight of

about 164. This is about twice the atomic weight of selenium, showing that the molecule of selenium, like the molecule of sulphur, contains at this temperature two atoms.

Compounds of Selenium. — Selenium combines directly with hydrogen, forming the compound H_2Se — *hydrogen selenide* — which is strictly analogous to hydrogen sulphide. This compound is also obtained when metallic selenides are treated with a strong acid.

Selenium combines with oxygen, forming *selenium dioxide*, the analogue of sulphur dioxide. This is a crystalline solid, which, when dissolved in water, forms selenious acid, of which it is obviously the anhydride. This is the only compound of oxygen and selenium which is known.

Selenious acid, formed by the union of selenium dioxide with water, —

$$SeO_2 + H_2O = H_2SeO_3,$$

resembles in many respects sulphurous acid. It forms two series of salts, the acid selenites and the selenites, having the compositions, respectively, $MHSeO_3$ and M_2SeO_3.

It differs, however, from sulphurous acid in not being a strong reducing agent. Indeed, it is not a reducing agent at all, but readily gives up its oxygen, and is therefore an oxidizing agent. When selenious acid is treated with sulphur dioxide, the former is reduced to selenium, and the latter oxidized to sulphuric acid.

While the compound selenium trioxide is not known, the acid corresponding to this anhydride is known. When selenium is treated with strong oxidizing agents, such as chlorine or bromine water, or metallic selenites treated with bromine or fused with potassium nitrate, *selenic acid* or its salt is formed. The acid is a solid, melting at 58°. Like sulphuric acid it combines with water, forming a hydrate, $H_2SeO_4 . H_2O$. Unlike sulphuric acid it is a strong oxidizing agent, readily giving up its oxygen and passing over to selenious acid or selenium.

Selenium combines with chlorine, forming two chlorides; selenium monochloride, Se_2Cl_2, and selenium tetrachloride, $SeCl_4$. The latter is a comparatively stable substance and thus differs from the corresponding chloride of sulphur. Selenium combines with sulphur, forming the compound SeS_2.

TELLURIUM (At. Wt. = 127.6)

Tellurium. — Tellurium is a much rarer element than selenium, occurring combined with such metals as lead, bismuth, silver, and

gold. Tellurium forms grayish-white crystals which resemble a metal. It conducts electricity and thus resembles one modification of selenium. Its melting-point is about 450°. Its boiling-point is 1400°. Its vapor-density shows a molecular weight which is twice its atomic weight. At this temperature there are, therefore, two atoms in the molecule, in this respect resembling sulphur and selenium.

Compounds of Tellurium. — Tellurium combines with hydrogen, forming *hydrogen telluride*, having the composition H_2Te. This is analogous to hydrogen sulphide and hydrogen selenide. It is a gas with a very disagreeable odor like the former compounds.

Tellurium *combines with oxygen*, forming the compounds TeO, TeO_2, and TeO_3. The last two are analogous to sulphur dioxide and sulphur trioxide, while the first has no analogue among the sulphur compounds. These oxides, however, show very little tendency to combine with water, and thus differ markedly from the corresponding oxides of sulphur and selenium.

Tellurium, however, forms two acids with hydrogen and oxygen. These are *tellurious* and *telluric acids*, having the compositions, respectively, H_2TeO_3 and H_2TeO_4.

Tellurium, unlike sulphur and selenium, also shows certain basic properties. It forms with nitric acid a basic nitrate, and thus differs fundamentally from sulphur and selenium.

Tellurium can also combine with chlorine and bromine, forming the compounds $TeCl_2$ and $TeCl_4$, and $TeBr_2$ and $TeBr_4$.

CHAPTER XIV

NITROGEN (At. Wt. = 14.04)

We now pass to another group of elements, the nitrogen group. This is group V in the Periodic System. The members of the nitrogen group are nitrogen, phosphorus, arsenic, antimony, and bismuth. We shall first take up nitrogen and study it in some detail on account of its importance chemically.

Occurrence and Preparation.—The chief source of nitrogen is the atmospheric air, which consists approximately of one-fifth oxygen and four-fifths nitrogen. Nitrogen exists also in many forms of living matter, and in the waters and soil in the form of compounds which are important for the growth of plants.

It can be prepared in fairly pure condition by removing the oxygen from atmospheric air. This can be accomplished by means of phosphorus. When moist phosphorus is brought in contact with the air, the oxygen combines with the phosphorus, forming phosphorus pentoxide, P_2O_5, and the nitrogen remains behind.

The oxygen can be removed from atmospheric air also by certain metals at an elevated temperature. Thus, when metallic copper is heated to redness in the presence of atmospheric air, the oxygen combines with the copper, forming cupric oxide, CuO, and the nitrogen remains behind. This method is used quite frequently in preparing fairly pure nitrogen upon the large scale, since the oxygen can be removed from a considerable volume of air in a comparatively short time by this method. The air is allowed to pass over the copper, which is heated to redness in a glass tube, and the nitrogen is collected as it escapes from the end of the tube.

Neither of the above methods is capable of yielding very pure nitrogen, since there is present in atmospheric air small quantities of many other substances, as we shall see; and none of these are removed by the phosphorus. They therefore remain and contaminate the resulting nitrogen. It is possible to prepare fairly pure nitrogen from atmospheric air, but this is a difficult and tedious operation.

To prepare nitrogen of a high degree of purity, certain chemical

reactions are made use of. When ammonium nitrite, a compound having the composition NH_4NO_2, is heated, the following reaction takes place: —

$$NH_4NO_2 = 2\,H_2O + N_2.$$

This is an excellent method of preparing pure nitrogen.

Another convenient method of obtaining pure nitrogen is by the action of nitrous acid, a compound having the composition HNO_2, upon urea, an organic compound containing nitrogen, and having the composition CON_2H_4: —

$$2\,HNO_2 + CON_2H_4 = CO_2 + 3\,H_2O + 2\,N_2.$$

Chemical Properties of Nitrogen. — Nitrogen is characterized by its inertness, not only at ordinary temperatures, but even at elevated temperatures. If we consider its chemical inactivity alone, we would be surprised that Rutherford discovered it as early as 1772. When we remember, however, that it constitutes four-fifths of our atmosphere, and that the oxygen can be separated from it, we can understand why it should have been discovered so early.

A few substances, however, combine with nitrogen at elevated temperatures, forming compounds known as *nitrides*. These include magnesium, boron, lithium, and silicon. On account of its chemical inactivity nitrogen cannot support combustion, except in the very few cases of substances which combine directly with nitrogen.

It cannot support life, all animals dying in a very short time when compelled to breathe only nitrogen. Nitrogen is taken into the lungs with every breath in quantities about four times as great as oxygen. On account of its chemical inactivity it does no harm to the organism, simply serving to dilute the oxygen.

Physical Properties of Nitrogen. — Nitrogen is a tasteless, odorless, colorless gas. Its critical temperature is $-146°$, and its critical pressure is 35 atmospheres. It can, therefore, be liquefied, but a very low temperature must be employed. It forms a colorless liquid, boiling at $-195°$. Nitrogen is liquefied by the same general methods as air. Indeed, liquid air is four-fifths liquid nitrogen. When liquid air evaporates, the nitrogen boils off first, as we have seen. The reason for this is now apparent. Nitrogen liquefies about thirteen degrees lower than oxygen, which is the same as to say that its boiling-point is thirteen degrees below that of oxygen. When a mixture of the two is allowed to evaporate, the lower-boiling liquid passes off more rapidly and leaves the higher-boiling liquid behind. Of course some of the liquid oxygen evaporates also, but the nitro-

gen evaporating more rapidly, finally leaves behind almost pure liquid oxygen. Liquid nitrogen, when allowed to evaporate under very small pressure, is an excellent refrigerating agent. It boils in a vacuum at from $-225°$ to $-230°$.

When liquid nitrogen is cooled to $-214°$, it solidifies. The melting-point is, therefore, above the boiling-point in a vacuum. When solid nitrogen is warmed in a vacuum, it would, therefore, pass at once into a vapor, without assuming the liquid state.

COMPOUNDS OF NITROGEN WITH HYDROGEN

Ammonia, NH_3.—The best-known compound of nitrogen and hydrogen is ammonia. Ammonia occurs in nature in small quantities in the free condition. It occurs in certain waters, in very small quantity in the atmosphere, and in certain minerals. In the form of its salts it occurs in many soils, and on account of their great solubility the salts of ammonia exist largely in solution in water. The salts of ammonia are very valuable in the soil in connection with the growth of plants, and efforts are continually being made to cause their accumulation in soils used for agricultural purposes. Ammonia is liberated in considerable quantity by decomposing organic matter. This is readily detected by the odor of the gas escaping from decomposing animal remains or decaying vegetable matter.

Ammonia can be formed in the laboratory by a number of methods. When nitric oxide is treated with nascent hydrogen, ammonia is formed:—

$$5\,H_2 + 2\,NO = 2\,H_2O + 2\,NH_3.$$

Ammonia can be formed by the direct union of hydrogen and nitrogen. When one part of nitrogen is mixed with three parts of hydrogen and electric sparks passed through the mixture, a part of the hydrogen and nitrogen combine, forming ammonia. The combination is far from complete, unless the ammonia is removed as fast as formed. In the latter case all of both gases can be made to combine:—

$$N_2 + 3\,H_2 = 2\,NH_3.$$

The volume of the ammonia formed is just half the sum of the volumes of the nitrogen and hydrogen which have disappeared. *If one volume of nitrogen combines with three volumes of hydrogen, there are two volumes of ammonia formed.*

This shows again the simple relations by volume in which gases

combine, and the simple relation between the volumes of the original gases and the volume of the product.

Ammonia is most conveniently prepared by the action of a base on an ammonium salt. When ammonium chloride, nitrate, or sulphate is boiled with an aqueous solution of a strong base like sodium hydroxide, ammonia gas is liberated: —

$$NH_4Cl + NaOH = NaCl + H_2O + NH_3;$$
$$NH_4NO_3 + NaOH = NaNO_3 + H_2O + NH_3;$$
$$(NH_4)_2SO_4 + 2\,NaOH = Na_2SO_4 + 2\,H_2O + 2\,NH_3.$$

In the laboratory ammonia is prepared most conveniently by mixing slaked lime with ammonium chloride and warming the mixture. The reaction is —

$$2\,NH_4Cl + Ca(OH)_2 = CaCl_2 + 2\,H_2O + 2\,NH_3.$$

Ammonia was formerly obtained from decaying organic matter, and from ammonium salts which occurred in certain arid regions of the earth. The ammonium chloride which occurred in the neighborhood of the temple of Jupiter Ammon was termed *sal ammoniac*, whence the origin of the name ammonia. Ammonia to-day is obtained mainly from the dry distillation of coal in the manufacture of illuminating gas. The ammonia liquor from the gas-works is treated with sulphuric acid, when ammonium sulphate is formed. In this form ammonia can be readily transported, and can be obtained in free condition from the sulphate by treating the latter with a strong base.

Chemical Properties of Ammonia. — Ammonia in the pure, dry condition is not active chemically. *When perfectly dry ammonia gas is brought in contact with perfectly dry hydrochloric acid gas, there is not the slightest reaction between the two substances.* If there is a mere trace of moisture present, the two gases react at once, forming the solid ammonium chloride.

Certain metals like sodium react with ammonia. When ammonia gas is passed over metallic sodium, the following reaction takes place: —

$$2\,NH_3 + Na = 2\,NH_2Na + H_2.$$

Ammonia dissolves in water with the greatest ease, forming a compound which neutralizes acids and which is, therefore, *a basic substance.* From the study of a large number of basic substances we are led unmistakably to the conclusion that all bases contain the

group (OH), known as hydroxyl; and when bases are dissolved in water this group splits off as the anion, and gives the basic character to the solution of the substance in question.

When ammonia dissolves in water, it must, therefore, combine with the water, forming the compound NH_4OH:—

$$NH_3 + H_2O = NH_4OH.$$

The compound NH_4OH, which, however, has never been isolated, is then acted on by more water, and dissociated thus:—

$$NH_4OH = \overset{+}{N}H_4, \overset{-}{O}H.$$

The hypothetical group NH_4 is called *ammonium*. While this group has not been isolated, there is little doubt as to its existence. It plays the same rôle, as we shall see, that a metal atom does in the formation of compounds.

Composition of Ammonia.—We have seen that one volume of nitrogen combines with three volumes of hydrogen, forming ammonia. From Avogadro's law, there are just as many ultimate particles or molecules in one volume of hydrogen as in one volume of nitrogen, therefore three times as many in three volumes of hydrogen. From a study of the densities of hydrogen and nitrogen, we have seen that the molecule of each substance is composed of two atoms. Therefore, in three molecules of hydrogen we have six atoms, and in one molecule of nitrogen two atoms. Since one volume of nitrogen combines with three volumes of hydrogen, then, to form ammonia, the molecule of ammonia must be NH_3 or some multiple of NH_3. By a vapor-density determination, we decide this part of the question and find that ammonia is NH_3.

This is the synthetical method of determining the composition of ammonia. There is also the analytical method.

When ammonia is treated with chlorine, it is decomposed into hydrochloric acid and nitrogen:—

$$2\,NH_3 + 3\,Cl_2 = 6\,HCl + N_2.$$

Chlorine combines with hydrogen volume for volume. It is therefore only necessary to know the volume of the chlorine used up, and the volume of the nitrogen set free when chlorine acts on ammonia, to know the volume of the hydrogen which was combined with the volume in question of the nitrogen to form ammonia.

A glass tube closed by means of a stop-cock, and containing above the stop-cock a reservoir for holding concentrated ammonia, is filled with pure chlorine. This tube is divided into three equal parts.

The concentrated ammonia is allowed to flow through the stop-cock drop by drop. When it comes in contact with the chlorine, the action is so vigorous that there is a flash of fire as each drop of ammonia enters the tube containing the chlorine. When ammonia has been admitted to the tube until all the chlorine is used up, shown by the fact that when more ammonia is added there is no further evidence of chemical action, some more ammonia is run in to combine with the hydrochloric acid which has been formed as the result of the reaction. When all the hydrochloric acid has combined with the ammonia, forming ammonium chloride, which dissolves in the aqueous ammonia, and the gas in the tube allowed to come to normal pressure by admitting water as long as the pressure of the air will drive it into the tube, the tube will be found to be exactly one-third full of nitrogen gas. The tube which was full of chlorine at atmospheric pressure has a volume which is just equal to that of the hydrogen which was combined with the nitrogen set free. This, we have seen, is one-third of the volume of the chlorine originally used, and, therefore, of the hydrogen with which the nitrogen was combined in the ammonia. Ammonia consists, then, of one volume of nitrogen combined with three volumes of hydrogen.

The equations expressing the reaction of ammonia on chlorine, and then on the hydrochloric acid formed, are —

$$3\,Cl_2 + 2\,NH_3 = 6\,HCl + N_2;$$
$$6\,HCl + 6\,NH_3 = 6\,NH_4Cl.$$

Physical Properties of Ammonia. — Ammonia is a colorless gas with a very penetrating odor. One litre of ammonia at 0° and 760 millimetres pressure weighs 0.775 grams. The critical temperature of ammonia is 130°, so that it can be easily liquefied. At 10° it is converted into a liquid when subjected to a pressure of 6.2 atmospheres. It boils under atmospheric pressure at $-33°.7$, and is converted into a solid which melts at $-78°.3$. *Liquid ammonia* is a very interesting substance. It has been shown to have considerable dissociating power. Solutions of salts dissolved in liquid ammonia conduct the electric current very well, and in some cases better than solution in water at the same concentrations. This does not mean that salts in liquid ammonia are dissociated to a greater extent than in water. Dissociation, as we have seen, depends upon the molecular conductivity μ_v, at any dilution, v, and also upon the molecular conductivity at complete dissociation, μ_∞. μ_v may be larger in liquid ammonia, and μ_∞ still larger for any substance in the ammonia, when the dissociation, α, which is the ratio between the two,

would be smaller in the ammonia than in water. Such being the case, μ_∞ is larger for a given substance in liquid ammonia than in water. The question arises, however, Why is μ_∞ larger in ammonia than in water? μ_∞ depends upon two quantities; the number of the ions present and the velocity with which they move. We have just seen that the number of ions present in the ammonia is less than in water, and must conclude, therefore, that the ions move with greater velocity in liquid ammonia than in water. There are methods available for measuring the relative velocities of ions, but these have not yet been applied to liquid ammonia.

Liquid ammonia has *a very high specific heat.* According to some authorities, slightly higher even than water. On account of its high heat of vaporization it is an excellent refrigerating agent, and is used extensively for this purpose, especially in connection with the *artificial preparation of ice.* Ammonia gas is liquefied by pressure, a large amount of heat being, of course, set free during the process. This heat is removed by a current of cold water flowing around the vessel in which the liquefaction is taking place. The liquid ammonia then flows into tubes which closely surround the vessels containing the water which is to be frozen, and is allowed to vaporize in these tubes. In vaporizing it must obtain heat from somewhere, and takes it from surrounding objects. The water loses its heat, is cooled below the freezing temperature, and solidifies. The ammonia, having passed into the form of a vapor, is not lost, but is pumped into the liquefying chamber, subjected again to pressure and liquefied, the heat set free being again removed by the current of cold water. The process is thus a continuous one, the same ammonia being used over and over again.

Machines for freezing water by means of liquid ammonia, were early devised by Carré and were known as *Carré ice machines.* Many of the modern devices are modifications of these machines of Carré, utilizing exactly the same principles.

A few years ago most of the "artificial ice" was made by the ammonia process. Now considerable ice is obtained by allowing water to evaporate into a space under diminished pressure.

Ammonia dissolves in water, as we have already seen. It is one of the most soluble of all known gases, one volume of water, at 0°, dissolving about 1150 volumes of ammonia. As the temperature rises, the solubility of the ammonia decreases very rapidly. Aqueous ammonia has a much smaller specific gravity than water, the specific gravity decreasing as the concentration of the solution increases. A few examples will make this clear: —

Percentage of Ammonia	Specific Gravity
1 per cent	0.996
5 per cent	0.979
10 per cent	0.959
25 per cent	0.911
30 per cent	0.898
36 per cent	0.884

At first it may not be perfectly clear how a concentrated solution of ammonia in water could be lighter than pure water. When ammonia dissolves in water there is a large increase in volume, and this more than compensates for the addition of the ammonia.

Ammonium, NH_4. — When ammonia dissolves in water, we have seen that it combines with a molecule of the water, in the sense of the following equation: —

$$NH_3 + H_2O = NH_4OH.$$

This compound, ammonium hydroxide, dissociates in the presence of more water into the ions ammonium and hydroxide: —

$$NH_4OH = \overset{+}{N}H_4, \overset{-}{O}H.$$

While the group ammonium has never been isolated, it acts as a unit in compounds which ammonia forms with acids. In its chemical properties it so closely resembles the alkali metals, that it is classed with them.

Ammonium Amalgam, NH_4Hg. — While the compound NH_4 has never been isolated, its amalgam, or compound with mercury, is readily prepared. When sodium amalgam, a compound of sodium and mercury having the composition NaHg, is treated with a concentrated solution of ammonium chloride, the amalgam swells up, occupying a relatively large volume. The product has a metallic lustre, and is probably ammonium amalgam. The reaction probably takes place in the sense of the following equation: —

$$NaHg + NH_4Cl = NaCl + NH_4Hg.$$

It would seem that ammonium amalgam was a hopeful substance from which to obtain the group ammonium. It is, however, unstable, breaking down at ordinary temperatures into ammonia, hydrogen, and mercury.

This is, apparently, the nearest that we have come thus far to obtaining the group ammonium in the free condition, but it is obvious

that the group is unstable under all the conditions to which it has thus far been subjected.

Hydrazine, N_2H_4. — A number of methods have been devised for preparing hydrazine. Some of these, however, involve a knowledge of organic chemistry and cannot be taken up in this place. One method of preparing hydrazine can, however, be referred to.

When potassium nitrite, a compound having the composition KNO_2, is treated with sulphurous acid, the two combine forming the compound $K_2SO_3N_2O_3$. When this is reduced by nascent hydrogen, hydrazine is formed: —

$$K_2SO_3N_2O_3 + 4\,H_2 = K_2SO_4 + 2\,H_2O + N_2H_4.$$

It is also formed by the reduction of hyponitrous acid $N_2O_2H_2$, by nascent hydrogen: —

$$N_2O_2H_2 + 3\,H_2 = 2\,H_2O + N_2H_4.$$

Properties of Hydrazine. — Hydrazine is a liquid boiling at 113°. It forms a crystalline solid which melts at 1°.4. It combines with water, forming the hydrate $N_2H_4 . H_2O$. Like ammonia, it has basic properties forming salts with acids.

Triazoic Acid, or Hydrazoic Acid, HN_3. — This remarkable compound was discovered a few years ago by the German chemist Curtius. The compound is remarkable on account of its composition and properties. It is surprising that we should have a compound containing three nitrogen atoms and a hydrogen atom, and nothing else. It is still more surprising that such a compound should have strongly acid properties.

Hydrazoic acid is prepared most simply by the action of nitrous oxide, N_2O, upon soda amide $NaNH_2$, formed as we have seen by the direct action of ammonia on metallic sodium: —

$$N_2O + 2\,NaNH_2 = NH_3 + NaOH + NaN_3.$$

When the sodium salt is treated with a strong acid, hydrazoic acid is formed: —

$$NaN_3 + HCl = NaCl + HN_3.$$

Hydrazoic acid is formed also by the action of nitrous acid on hydrazine: —

$$HNO_2 + N_2H_4 = 2\,H_2O + HN_3.$$

Also by the action of an oxydizing agent on a mixture of hydrazine and hydroxyl amine: —

$$N_2H_4 + NH_3O + O_2 = 3\,H_2O + HN_3.$$

Hydrazoic acid is a colorless liquid, boiling at 37°. It is very explosive in concentrated solution, and its fairly dilute, aqueous solution must be dealt with carefully or explosion will result. It is a strong acid, its aqueous solutions readily conducting the electric current. It dissolves many of the metals, forming salts, which resemble in general the chlorides, differing from them, however, in being very explosive. The composition of the salts is as remarkable as that of the acid itself. The salts with the univalent metals consist of a metal atom united with three nitrogen atoms. When we consider the inertness of nitrogen, it is surprising that such a compound should be capable of existence. The *ammonium salt* has the composition $HN_3.NH_3 = N_4H_4$, and is another compound of hydrogen and nitrogen. The base *hydrazine combines with triazoic acid, forming the compound* $N_2H_4.HN_3 = N_5H_5$, a fifth compound of nitrogen and hydrogen. The five compounds of hydrogen and nitrogen which are thus far known have, respectively, the compositions: —

NH_3	N_3H	N_5H_5.
N_2H_4	N_4H_4	

CHAPTER XV

NEUTRALIZATION OF ACIDS AND BASES

Ammonium Hydroxide. — We have seen that when the compound ammonia is dissolved in water, it combines with the water, forming ammonium hydroxide: —

$$NH_3 + H_2O + NH_4OH.$$

Ammonium hydroxide dissociates as follows: —

$$NH_4OH = \overset{+}{NH_4}, \overset{-}{OH}.$$

Ammonium hydroxide when dissolved in water dissociates into the cation ammonium and the anion hydroxyl. The hydroxyl ion and not the ammonium ion gives the characteristic basic property to the solution. This is shown by the fact that there are many compounds which, when dissolved in water, dissociate yielding the ammonium ion, and these solutions have no basic properties. On the other hand, every compound which yields hydroxyl ions is a basic substance.

Bases are Hydroxyl Compounds. — That the statement is correct that bases are hydroxyl compounds, can be seen at once by examining the composition of a number of basic substances.

Ammonium hydroxide	NH_4OH
Sodium hydroxide	$NaOH$
Potassium hydroxide	KOH
Calcium hydroxide	$Ca(OH)_2$
Strontium hydroxide	$Sr(OH)_2$
Barium hydroxide	$Ba(OH)_2$
Aluminium hydroxide	$Al(OH)_3$
Ferric hydroxide	$Fe(OH)_3$

This list of basic substances could be greatly extended. It will be observed that they all contain a metal combined with one or more hydroxyl groups. When these substances dissociate, the hydroxyls split off as anions, and the metal forms the cation. A few examples will make this clear: —

$$NaOH = \overset{+}{Na}, \overset{-}{OH}.$$
$$KOH = \overset{+}{K}, \overset{-}{OH}.$$
$$Ca(OH)_2 = \overset{++}{Ca}, \overset{-}{OH}, \overset{-}{OH}.$$
$$Ba(OH)_2 = \overset{++}{Ba}, \overset{-}{OH}, \overset{-}{OH}.$$
$$Al(OH)_3 = \overset{+++}{Al}, \overset{-}{OH}, \overset{-}{OH}, \overset{-}{OH}.$$

Acidity of Bases and Basicity of Acids. — We observe in the above examples that some bases dissociate yielding one hydroxyl ion, other bases yield two hydroxyl ions, and others still three hydroxyl ions. If we take a gram-molecular weight (the molecular weight of the substance in grams) of a monobasic acid and dissolve it in water, diluting the solution to a litre, and take a gram-molecular weight of any one of the above bases which yield one hydroxyl ion and dissolve it so as to form a litre of solution, the litre of the acid would exactly neutralize the litre of the base. Such a base which yields on dissociation one hydroxyl ion is known as a *monacid base:* —

$$\overset{+}{H}, \overset{-}{Cl} + \overset{+}{Na}, \overset{-}{OH} = H_2O + \overset{+}{Na}, \overset{-}{Cl}.$$

If we prepare a solution of a base which dissociates into two hydroxyl ions, containing a gram-molecular weight in a litre, it will require just two litres of a solution of an acid such as that referred to above to neutralize the one litre of the base: —

$$\overset{++}{Ca}, \overset{-}{OH}, \overset{-}{OH} + \overset{+}{H}, \overset{-}{Cl} + \overset{+}{H}, \overset{-}{Cl} = 2\,H_2O + \overset{-}{Cl}, \overset{-}{Cl}, \overset{++}{Ca}.$$

Such bases are known as *diacid bases.* To neutralize a gram-molecular weight of a base which dissociates into three hydroxyl ions, requires just three litres of the above solution of acid. Such a base is termed a *triacid base:* —

$$\overset{+++}{Al}, \overset{-}{OH}, \overset{-}{OH}, \overset{-}{OH} + \overset{+}{H}, \overset{-}{Cl} + \overset{+}{H}, \overset{-}{Cl} + \overset{+}{H}, \overset{-}{Cl} =$$
$$3\,H_2O + \overset{+++}{Al}, \overset{-}{Cl}, \overset{-}{Cl}, \overset{-}{Cl}.$$

A solution containing a gram-molecular weight of a substance in a litre is known as a *molecular normal* solution. A solution which contains in a litre a gram-molecular weight of the substance divided by its valence is known as an *equivalent normal* solution. When we are dealing with a monacid base, the two solutions are identical. When the base is diacidic, we must divide its molecular weight by two and dissolve this number of grams so as to form a litre of solution, in order to have an equivalent normal solution. In such a case

the equivalent normal solution is just half as strong as the molecular normal. In the case of a triacid base, the equivalent normal is one-third of the molecular normal, and so on.

The terms molecular normal and equivalent normal solutions are used continually, and their meaning should be clearly understood.

Just as we have mono-, di-, and tri-acid bases, just so we have mono-, di-, and tri-basic acids. An acid which dissociates, yielding one hydrogen ion, is *monobasic:* —

$$HCl = \overset{+}{H}, \overset{-}{Cl}.$$

If the molecule of the acid yields two hydrogen ions, it is *dibasic:* —

$$H_2SO_4 = \overset{+}{H}, \overset{+}{H}, \overset{=}{SO_4}.$$

If the molecule of the acid dissociates, yielding three hydrogen ions, it is *tribasic:* —

$$H_3AsO_4 = \overset{+}{H}, \overset{+}{H}, \overset{+}{H}, \overset{\equiv}{AsO_4};$$

and so on.

Indicators. — In neutralizing acids with bases, we must use some means to determine when there is no longer any of the acid present, or any of the base present. We make use of certain color changes which are produced in certain substances by acids, on the one hand, and by bases on the other. If to a solution which contains an acid a little of the vegetable dye, litmus, is added, the litmus turns red, while in an alkaline solution it is blue. By adding cautiously a little acid to the alkali, or a little alkali to the acid, until the excess of the other is just neutralized, we have the neutral tint of the litmus, which is purple.

Similarly, methyl orange is colorless or slightly yellow in alkaline solution, and deep red in a solution which is acid. Phenolphthaleïn is red in the presence of an alkali, and colorless in the presence of an acid. Cyanine is blue in the presence of a base and colorless in the presence of an acid.

We understand pretty thoroughly the action of these indicators, now that we have the theory of electrolytic dissociation.

Theory of Indicators. — Chemical molecules may be colored or colorless, and ions may be colored, giving their color to completely dissociated solutions. A molecule may have the same color as the ions into which it dissociates, or it may have a different color. A colorless molecule may dissociate into ions, one or more of which is colored, and a colored molecule may dissociate into colorless ions.

Upon these facts is based the use of indicators in quantitative

analysis. An indicator is a compound which shows a change of color when the solution passes from the acid to the basic condition, and *vice versa.* An indicator is always either a weak acid or a weak base, which, on dissociation, yields an ion which has a different color from the molecule itself. Indicators fall then, naturally, into two classes, — acidic indicators and basic indicators. As an example of an *acidic indicator,* we will take first *phenolphthaleïn.* This is a weak acid, which means that in the presence of water it is very slightly dissociated, if it is dissociated at all. The molecules of phenolphthaleïn are colorless, as is shown by the fact than an aqueous or alcoholic solution of this substance is colorless. If a solution of a strong base is added to phenolphthaleïn, the salt of that base is formed. This salt, like most salts, is readily dissociated in the presence of water. The salt of phenolphthaleïn dissociates into the cation of the base and the complex organic anion; *e.g.* the sodium salt dissociates into the cation sodium and the complex organic anion; and it is this latter which gives the characteristic color of this indicator.

In using this indicator, a small quantity is brought into the presence of the acid, which is to be titrated against a strong base. The indicator, in the presence of pure water, is almost completely undissociated. In the presence of the strong acid, which contains many free hydrogen ions, it would be dissociated even less than in pure water, as we shall learn. An alkali is added and the strong acid is all neutralized. The moment an excess of alkali is present, it forms a salt with the phenolphthaleïn. This salt dissociates at once, and the colored anion gives its characteristic color to the solution.

Phenolphthaleïn cannot be used with weak acids nor weak bases. If the acid is so weak that its salts, even with strong bases, are *hydrolyzed, i.e.* broken down by water into the free acid and the free base, the free base would begin to react with the phenolphthaleïn long before enough base had been added to completely neutralize the acid. The result would be the appearance of a faint color on the addition of a little alkali, and this color would increase in intensity as more and more alkali was added. There would, then, be no sharp change in color when all the acid had been neutralized, and the indicator would be practically worthless in such cases. Thus, carbonic and phosphoric acids and the phenols cannot be titrated with phenolphthaleïn as an indicator. If a weak base is used, such as ammonia, there will also be a certain amount of hydrolysis of the salt. This will leave some free base present, which will react with the phenolphthaleïn and give rise to a gradual change in color. But even

if the ammonium salt of the acid which is being titrated is not hydrolyzed by water, ammonia cannot be used with phenolphthaleïn. Ammonia is a weak base, and phenolphthaleïn is a weak acid, and the salt of the two would itself be hydrolyzed by water. The indicator would, therefore, not act sharply when ammonia was used as a base.

It is well known that the facts agree very satisfactorily with the theory. Phenolphthaleïn cannot be used as an indicator with either weak acids or weak bases.

Another example of an acid indicator whose molecules are nearly colorless and whose anion is colored, is *p-nitrophenol.* In alcoholic solution, in which the substance is almost undissociated, it is nearly colorless. Water dissociates it slightly, and consequently the aqueous solution is slightly colored. If an alkali is added, the salt of this weak acid is formed, and this dissociates into the metallic cation, and into the anion $C_6H_4(NO_2)O$, which is deep yellow in color. The action of this substance as an indicator will be understood at once from the above description of the action of phenolphthaleïn.

Litmus is an example of an acid indicator whose molecules are colored, but whose anion has a different color. The molecules of the weak litmus acid are red. When an alkali is added the salt is formed, and this dissociates giving the free litmus anion, which is deep blue. Litmus, like phenolphthaleïn, cannot be used satisfactorily with weak bases. These would form salts with the litmus, which would be hydrolyzed and prevent a sharp color reaction; or their salts, with any but the strongest acids, would undergo some hydrolysis and prevent a sharp appearance of color. In order that litmus should be used in titrating weak acids, only the strongest bases can be employed.

An acid indicator which can, however, be used with weak bases is *methyl orange.* This is a considerably stronger acid than the indicators which we have already considered. The molecules of the free acid are red, the anions yellow. In the presence of a strong acid we have, therefore, the characteristic red color; while in the presence of a base the salt is formed, and this dissociates, yielding the yellow anion. This indicator can be used with weak bases, provided they are titrated with strong acids. In these cases there is but slight hydrolysis of the salts formed, and also but slight hydrolysis of the salt formed by the methyl orange and the weak base, since the indicator is a fairly strong acid.

In the above discussion of acid indicators it will be seen that weak acids must always be titrated with strong bases, and a weakly acid indicator may be employed.

Weak bases, on the other hand, must be titrated with strong acids, and a strongly acid indicator must be used.

Basic indicators are but little used in practice. As an example of this class we may take *cyanine*. This is a weak base, and, therefore, but little dissociated. The molecules are deep blue in color. In the presence of an acid a salt is formed, which dissociates into the anion of the acid and the cation of the base. This very complex cation is colorless; consequently, the indicator is blue in the presence of a base, and colorless in the presence of an acid.

The examples considered above suffice to illustrate the different types of indicators, and to show how satisfactorily their action is explained in terms of the theory of electrolytic dissociation.

Salts. — When a dilute solution of an acid acts on a dilute solution of a base, what takes place and all that takes place is the formation of a molecule of water: —

$$\overset{-}{Cl}, \overset{+}{H} + \overset{-}{OH}, \overset{+}{Na} = H_2O + \overset{-}{Cl}, \overset{+}{Na}.$$

The sodium ion remains after the process of neutralization in exactly the same condition as before, and, similarly, the chlorine remains in the ionic condition. The hydrogen and hydroxyl ions, however, unite and form a molecule of water. It is a general rule that, *whenever we have hydrogen and hydroxyl ions in the presence of one another uncombined, they unite and form water.* There is an abundance of direct experimental evidence in favor of this conclusion.

If, however, we evaporate the solution containing the sodium and chlorine ions, they unite and form a molecule of sodium chloride. This is a salt. We would define a salt as follows: *A salt is a compound formed by the union of an anion of an acid with a cation of a base.* This takes place generally, as already stated, only when the solution containing these ions is evaporated and at least a part of the water removed.

The salts are named after the acids from which they are derived. Salts of hydrochloric acid are called chlorides, those of nitric acid nitrates, and those of sulphuric acid sulphates. In general, salts of acids which end in "*ic*" are termed "*ates*"; salts of sulphurous acid are called sulphites, salts of nitrous acids nitrites, and so on. In general, salts of acids which end in "*ous*" end in "*ite.*"

So much for the nomenclature of salts in terms of the acids. Since the cation also enters into the salt, we must be able to distinguish the salts of one cation from the salts of another cation. The name of the cation is used before the name of the acid with whose salt we are dealing. Thus, the chloride of sodium is known as

sodium chloride, the chloride of calcium, calcium chloride, and so on. When we come to metals which show different valence the case is a little more complicated.

Take the case of copper. It forms two chlorides — $CuCl$ and $CuCl_2$. The former, in which the copper is monovalent, is known as cuprous chloride, and the latter cupric chloride. Take the two chlorides of iron — $FeCl_2$ and $FeCl_3$. The former is known as ferrous chloride and the latter as ferric chloride. It is a general rule that the name of the salt in which the metal has the lower valence, *i.e.* carries the smaller electrical charge, ends in *ous*, while the name of the salt in which the metal has the higher valence ends in *ic*.

One further point in connection with the nomenclature of salts must be mentioned. If we are dealing with a dibasic acid, there are two possibilities. We may have a salt still containing one of the hydrogen atoms of the acid, as $KHSO_4$, $KHSO_3$, etc. These are known as acid potassium sulphate and acid potassium sulphite, while the salts K_2SO_4 and K_2SO_3 are known as normal potassium sulphate and normal potassium sulphite. The acid salts are also frequently known as primary salts — primary potassium sulphate and primary potassium sulphite.

When we are dealing with salts of tribasic acids, we have three possibilities, and in many cases they are all realized. Take phosphoric acid, H_3PO_4; we can have three salts with a univalent cation: —

$$KH_2PO_4,\ K_2HPO_4,\ \text{and}\ K_3PO_4.$$

The first is known as monopotassium phosphate, or primary potassium phosphate; the second as dipotassium phosphate, or secondary potassium phosphate; and the third as normal potassium phosphate.

There is still a class of salts which we have not considered. Just as we may have acid salts in which part of the acid hydrogen remains, so we may have *basic salts,* in which part of the unneutralized hydroxyls remain. Take bismuth hydroxide; there are three nitrates having the compositions: —

$$Bi(OH)_2NO_3,\ BiOH(NO_3)_2,\ \text{and}\ Bi(NO_3)_3.$$

These are known as bismuth mononitrate, bismuth dinitrate, and bismuth trinitrate or the normal nitrate of bismuth.

Having considered the nomenclature of salts at sufficient length, we shall pass to the study of the energy changes which take place when an acid is neutralized by a base.

Heat of Neutralization. — When solutions of acids and bases are brought together, heat is liberated. Quantitative measurements of the amounts of heat set free brought out a simple and very important relation. This can best be seen from the following results for strong acids and bases. Gram-molecular weights of different acids were brought together with a gram-molecular weight of a given base, both the acid and base being present in very dilute solution. The amounts of heat set free by a number of acids when neutralized with the base sodium hydroxide, were: —

	Heat of Neutralization
Hydrochloric acid and sodium hydroxide	13,700 cals.
Hydrobromic acid and sodium hydroxide	13,700 cals.
Nitric acid and sodium hydroxide	13,700 cals.
Hydriodic acid and sodium hydroxide	13,800 cals.
Chloric acid and sodium hydroxide	13,760 cals.
Bromic acid and sodium hydroxide	13,780 cals.
Iodic acid and sodium hydroxide	13,810 cals.

The remarkable fact comes out that the heat of neutralization of these strong acids with a given base, sodium hydroxide, is a constant.

This suggests a further question very closely correlated to the above. Suppose we neutralize a given acid with a number of bases, will the heat liberated be a constant? and if so, will this bear any close relation to the above constant where the base was the same and the acid changed? This can be answered by the following results, in which hydrochloric acid was neutralized by a number of bases: —

	Heat of Neutralization
Hydrochloric acid and lithium hydroxide	13,700 cals.
Hydrochloric acid and potassium hydroxide	13,700 cals.
Hydrochloric acid and barium hydroxide	13,800 cals.
Hydrochloric acid and calcium hydroxide	13,900 cals.

The heat of neutralization of a given acid with a number of bases is also a constant, provided the acid and bases are present in very dilute solution. But what is even more surprising, the constant in this case has the same value as in the preceding case where the base was unchanged, and the nature of the acid varied.

These facts when they were first discovered were very perplexing. Indeed, no satisfactory explanation of them could be furnished, and it was not until the theory of electrolytic dissociation was proposed that we could account for them at all.

Explanation of the Constant Heat of Neutralization of Strong Acids and Strong Bases. — It is one of the crowning glories of the theory of electrolytic dissociation, that it not only explains all of the facts in connection with the neutralization of strong acids and bases in dilute aqueous solution; but these facts are a necessary consequence of the theory.

Take, as an example, hydrochloric acid and sodium hydroxide. In a very dilute, aqueous solution of hydrochloric acid all the molecules are dissociated into hydrogen and chlorine ions thus: —

$$HCl = \overset{+}{H} + \overset{-}{Cl}.$$

Similarly, in dilute aqueous solution the molecules of sodium hydroxide are completely broken down into ions: —

$$NaOH = \overset{+}{Na}, \overset{-}{OH}.$$

When the dilute aqueous solutions of the base and acid are brought together, the following reaction takes place: —

$$\overset{+}{Na}, \overset{-}{OH} + \overset{+}{H}, \overset{-}{Cl} = \overset{+}{Na}, \overset{-}{Cl} + H_2O.$$

The cation of the base, sodium, and the anion of the acid, chlorine, remain in solution as ions after the process of neutralization in exactly the same condition as before neutralization took place. The anion of the base, hydroxyl, and the cation of the acid, hydrogen, combine and form a molecule of water.

It may be urged that the sodium and chlorine ions combine, since sodium chloride is formed as the result of the neutralization. The salt is formed if the solution is evaporated; *i.e.* if the solution is concentrated. But it can be shown by several separate and independent methods, that a dilute solution of sodium chloride contains only ions and no molecules. The sodium and chlorine, then, remain as ions.

The hydrogen and hydroxyl combine and form a molecule of water. This is proved by the fact that water is always formed as the result of the process of neutralization; and further, it has been shown by a half-dozen different methods that hydrogen and hydroxyl ions cannot remain in the presence of one another uncombined to any appreciable extent. This is the same as to say that water is practically undissociated.

Since hydroxyl is the anion of every base, and hydrogen the cation of every acid, the process of neutralization of any strong acid with any strong base in dilute solution, consists in the union of the hydroxyl ion of the base with the hydrogen ion of the acid, forming a molecule of water.

The process of neutralization of any acid by any base is, therefore, exactly the same as the process of neutralization of any other acid by any other base. The total heat that is liberated when a gram-equivalent of a completely dissociated acid acts on a gram-equivalent of a completely dissociated base, is the heat set free by the union of a gram-equivalent of hydroxyl ions with a gram-equivalent of hydrogen ions. Thus: —

$$\overset{+}{H}\,aq + \overset{-}{OH}\,aq = 13{,}700 \text{ cals.}$$

Since all processes of neutralization of completely dissociated acids and bases are the same, the heat of neutralization of all such acids and bases must be a constant, and must be the heat of combination of a gram-equivalent of hydroxyl and hydrogen ions.

Neutralization of Weak Acids and Bases. — If either the acid or base is what we term weak, the heat of neutralization is not 13,700 calories, but differs from this value. Thus, take the following examples: —

	Heat of Neutralization
Formic acid and sodium hydroxide	13,400 cals.
Acetic acid and sodium hydroxide	13,300 cals.
Dichloracetic acid and sodium hydroxide	14,830 cals.
Valeric acid and sodium hydroxide	14,000 cals.
Phosphoric acid and sodium hydroxide	14,830 cals.

In these cases the acids are weak and the base is strong; nevertheless, there are considerable differences between the heats of neutralization and the constant 13,700 calories.

Similar results were obtained when weak bases were neutralized with a strong acid. If, however, both acid and base are weak, the heat of neutralization differs still more from the constant 13,700 calories. A few examples of this condition are given below: —

	Heat of Neutralization
Formic acid and ammonium hydroxide	11,900 cals.
Acetic acid and ammonium hydroxide	11,900 cals.
Valeric acid and ammonium hydroxide	12,700 cals.

When the weak base ammonia is neutralized by the weak organic acids, the heat of neutralization differs very widely from the constant 13,700.

Explanation of the Results with Weak Acids and Bases. — If the acid or base is weak, we shall learn that it is only little dissociated by water, even in dilute solutions. When only a part of the acid or

base is dissociated, the process of neutralization could proceed only until all the dissociated substance had reacted; were it not for the fact that as soon as the ions already present begin to react, more ions would be formed from the undissociated molecules, or, in a word, the process of dissociation would continue as the reaction continued until all the molecules had dissociated.

When molecules dissociate into ions, heat is either evolved or consumed. The thermal change which accompanies the dissociation of the undissociated molecules, either increases or diminishes the amount of heat set free due to neutralization alone. If the heat of dissociation is positive, it adds itself to the heat of neutralization; if negative, it diminishes the heat of neutralization. Thus, the heat which is liberated when a weak acid acts on a weak base, may be either greater or less than the constant 13,700 calories — greater, when the heat of dissociation is positive, less, when it is negative. It could be equal to the constant only when the heat of dissociation is zero.

The facts, then, agree with the theory, not only when the acid and base are completely dissociated, but when the dissociation is not complete. We could predict from the theory of electrolytic dissociation that the heats of neutralization of weak acids and bases would not be a constant, with the same certainty that we could predict the constant value of the heats of neutralization of completely dissociated acids and bases. The apparent exceptions presented by the weak acids and bases furnish as strong confirmation of the theory as the cases which conform to rule.

Explanation of the Law of the Thermoneutrality of Solutions of Salts. — The theory of electrolytic dissociation furnishes us with the first rational explanation of the law of the thermoneutrality of salt solutions. This law, which was discovered by Hess, states that when dilute solutions of salts are mixed, there is little or no change in the heat tone. This is a necessary consequence of our theory. Take two salts, sodium chloride and potassium bromide. In dilute aqueous solutions these exist entirely as ions: —

$$NaCl = \overset{+}{Na}, \overset{-}{Cl},$$

$$KBr = \overset{+}{K}, \overset{-}{Br}.$$

When the solutions of these salts are mixed, all of the parts remain in solution as ions. There is no chemical action whatsoever, every constituent remaining in the same condition after mixing as before. There is, then, absolutely no reason to expect any thermal change, and none results.

We can now begin to see the importance and wide-reaching significance of the theory of electrolytic dissociation. This theory furnishes us with the explanation of the constant heat of neutralization of acids and bases, and of the law of the thermoneutrality of salts; and this is but the beginning. We shall see as our subject develops, that it has thrown an entirely new light on a great number of chemical problems which, without its aid, were simply empirically established facts, whose meaning was entirely shrouded in darkness. We shall see that this theory is fundamental, if we hope to raise chemistry from empiricism to the rank of an exact science.

COMPOUNDS OF NITROGEN WITH OXYGEN AND HYDROGEN

Ammonium Hydroxide, NH_4OH. — We have already seen that ammonium hydroxide is a basic substance. This is a compound of nitrogen with oxygen and hydrogen, and must be considered here. The most characteristic property of this substance is its basic nature. Being a base, it readily neutralizes acids, forming salts. Ammonium hydroxide unites readily with hydrochloric acid, forming a well-characterized, beautifully white salt, ammonium chloride: —

$$\overset{+}{N}H_4, \overset{-}{O}H + \overset{+}{H}, \overset{-}{Cl} = H_2O + \overset{+}{N}H_4, \overset{-}{Cl}.$$

As the water is removed, the ammonium and chlorine ions combine, forming ammonium chloride: —

$$\overset{+}{N}H_4, \overset{-}{Cl} = NH_4Cl.$$

Ammonium chloride or sal ammoniac, it will be remembered, is of special interest in connection with the determination of vapor-densities. It was one of those substances which gave abnormally low vapor-densities, and was for a long time regarded as an exception to the law of Avogadro. It will be recalled how it was proved experimentally that when ammonium chloride is heated it breaks down in the form of vapor into ammonia and hydrochloric acid, and was shown to present no real exception to the law of Avogadro. Ammonium hydroxide reacts readily with nitric acid, forming ammonium nitrate, and with sulphuric acid, forming ammonium sulphate. In the last case there are two possibilities. If there is sufficient ammonium hydroxide present, the normal sulphate is formed: —

$$2\,NH_4OH + H_2SO_4 = (NH_4)_2SO_4 + 2\,H_2O.$$

If there is only one equivalent of ammonium hydroxide present to one equivalent of sulphuric acid, the acid sulphate is formed:—

$$NH_4OH + H_2SO_4 = NH_4HSO_4 + H_2O.$$

While ammonium hydroxide has basic properties, it is not a strong base. Indeed, in comparison with such substances as sodium hydroxide and potassium hydroxide, it is a very weak base. The strength of a base, like the strength of an acid, is measured by its conductivity. Strength is proportional to dissociation, and dissociation is the ratio between the molecular conductivity of any dilution, μ_v, and the molecular conductivity at infinite dilution, μ_∞. $\alpha = \frac{\mu_v}{\mu_\infty}$.

The values of μ_v for several dilutions of ammonium hydroxide are given below:—

v	μ_v (18°)	a
2	1.2	0.5 per cent
10	3.1	1.4 per cent
100	9.2	4.4 per cent
1000	26.0	10.2 per cent
10,000	61.1	27.8 per cent
50,000	70.0	31.9 per cent
μ_∞	(220) ?	

To determine the value of μ_∞ for a weakly dissociated substance like ammonium hydroxide, we cannot proceed as already described, *i.e.* increase the dilution of the solution until on further increase the molecular conductivity does not change. The reason is that the dilution at which complete dissociation is reached is so great that the conductivity method cannot be applied to it. An indirect method must be employed in such cases.

Measurement of the Dissociation of a Weak Base, like Ammonium Hydroxide.—The difficulty encountered is in the determination of the value of μ_∞. While ammonium hydroxide itself is only slightly dissociated, the salts of this base are strongly dissociated, and, indeed, completely dissociated at dilutions to which the conductivity method can be readily applied. It is, then, a simple matter to determine the value of μ_∞ for an ammonium salt. The question which remains is, What connection exists between the value of μ_∞ for an ammonium salt and μ_∞ for the free base ammonia?

The answer is to be found in the *Law of Kohlrausch*, which says

that *the value of μ_∞ for any compound is the sum of two constants — the one depending on the anion and the other on the cation.* The value of μ_∞ for a salt like ammonium chloride is, then, the sum of two constants, a and b, a depending for its numerical value upon the cation $\overset{+}{N}H_4$, and b for its numerical value upon the anion $\overset{-}{Cl}$. We determine by the conductivity method the value of $\mu_\infty = a + b$. We know b (70.2) from prevous determinations and obtain a thus: —

$$a = \mu_\infty - b.$$

Ammonium hydroxide has exactly the same cation as ammonium chloride, $\overset{+}{N}H_4$, and, therefore, the value of a is the same for both compounds. Ammonium hydroxide is made up of the cation ammonium, whose conductivity constant is a, and the anion $(\overset{-}{O}H)$, whose conductivity constant we will call c. We know the numerical value of c from previous determinations, and determine the value of μ_∞ for ammonium hydroxide by adding a and c: —

$$\mu_\infty \text{ (for ammonium hydroxide)} = a + c.$$

If we are dealing with a weak acid, we use in a similar manner the salt of that acid with a strong base. The value of μ_∞ for the salt is determined. From this the constant for the cation of the salt is subtracted, and to the remainder the constant for hydrogen is added.

Hydroxylamine, $NH_2(OH)$. — The other compound of nitrogen with oxygen and hydrogen which has basic properties, is hydroxylamine. Although this compound was discovered in 1865, it was prepared in the pure condition for the first time in 1891 by Lobry de Bruyn.

Hydroxylamine is prepared by the direct action of nascent hydrogen on nitric oxide: —

$$3\,H_2 + 2\,NO = 2\,NH_2OH.$$

It is also prepared by the reduction of nitric acid by nascent hydrogen: —

$$HNO_3 + 3\,H_2 = 2\,H_2O + NH_2OH.$$

It consists of white needles, which, when exposed to moist air, take up water readily. It is, therefore, a *hygroscopic* substance. It melts at 33° and boils under 60 millimetres pressure at 70°.

Hydroxylamine dissolved in water has basic properties. This is the same as to say that it is dissociated by the water, yielding hydroxylions. Its conductivity shows that hydroxylamine is, how

ever, only a weak base. With acids it forms salts by simple addition, like ammonium hydroxide: —

$$NH_2OH + HCl = NH_3OHCl,$$
$$2\,NH_2OH + H_2SO_4 = (NH_3OH)_2SO_4.$$

Hydroxylamine is a strong reducing agent. Mercuric chloride is reduced to mercurous chloride, and an alkaline solution of a copper salt is reduced to cuprous oxide.

Hydroxylamine is reduced by nascent hydrogen, forming ammonia and water: —

$$NH_2OH + H_2 = H_2O + NH_3.$$

Compounds of Nitrogen with Oxygen. — Nitrogen forms the following compounds with oxygen: Nitrous oxide, N_2O; nitric oxide, NO; nitrogen sesquioxide or trioxide, N_2O_3; nitrogen dioxide or tetroxide, depending upon whether it has the composition NO_2 or N_2O_4; and nitrogen pentoxide, N_2O_5.

We shall now study these compounds in some detail.

Nitrous Oxide, N_2O. — Nitrous oxide is formed when ammonium nitrate is heated to 250°. The following equation expresses the reaction which takes place: —

$$NH_4NO_3 = 2\,H_2O + N_2O.$$

The oxygen and hydrogen combine and form water, and the nitrogen and oxygen form the compound N_2O, which escapes.

Nitrous oxide is a remarkable substance, in that it supports combustion almost as well as pure oxygen. Phosphorus and carbon burn readily in nitrous oxide. Certain substances, however, burn in oxygen and burn less readily or do not burn in nitrous oxide. The products of combustion in nitrous oxide are the same as in pure oxygen, showing that the compound, N_2O, is readily broken down, yielding free oxygen.

When nitrous oxide is inhaled into the lungs, it produces a remarkable physiological effect, generally throwing the subject into a hysterical condition. It is, therefore, known as *laughing gas*. When consumed in larger quantity it produces anesthesia, and is consequently used in minor surgical operations.

Nitrous oxide is a colorless gas, with a sweetish taste, and dissolves readily in cold water. It should, therefore, be collected in cylinders over hot water. Its critical temperature is 39°, and critical pressure 36 atmospheres. It liquefies under atmospheric pressure at −87°, and solidifies at −115°. When boiled under diminished

pressure, temperatures as low as $-135°$ to $-140°$ can be produced. In the liquid form it is an excellent refrigerating agent.

In reference to the energy changes which take place during chemical reactions, we meet here for the first time with a new condition. When most chemical reactions take place, heat is evolved, — most reactions are exothermic. In this case the opposite is true. When nitrogen and oxygen combine to form nitrous oxide, heat is absorbed. Such chemical reactions, which take place with absorption of heat, are known as *endothermic reactions*.

Nitric Oxide, NO. — Nitric oxide can be formed by the reduction of the higher oxides of nitrogen, or by the reduction of nitrous or nitric acid. It is prepared most conveniently by the action of nitric acid on metallic copper. The equation expressing the reaction is: —

$$8\ HNO_3 + 3\ Cu = 4\ H_2O + 3\ Cu(NO_3)_2 + 2\ NO.$$

As quickly as the colorless gas, nitric oxide, is brought in contact with free oxygen, the two combine at ordinary temperature: —

$$2\ NO + O_2 = 2\ NO_2.$$

The gas NO_2, as we shall learn, has a yellowish brown color, and as quickly as nitric oxide is brought in contact with the air, the above reaction takes place, giving the characteristic colored fumes. These are the fumes which always appear when nitric acid acts on metallic copper.

Nitric oxide not only has a remarkable power to combine with oxygen, forming a higher oxide of nitrogen, but also the power of giving up some of the oxygen which it already possesses, — of being an oxidizing agent. Certain substances, like phosphorus and magnesium, if once ignited, will continue to burn in nitric oxide, forming oxides with the oxygen obtained from nitric oxide. All of the oxygen is removed by metallic potassium or metallic sodium, free nitrogen remaining. Nitric oxide produces a dark, violet color when brought in contact with a warm solution of a ferrous salt. This reaction is used to detect nitric oxide.

Nitric oxide is a colorless gas, whose critical temperature is $-93°.5$, and whose critical pressure is 71.2 atmospheres. Its boiling-point is $-153°.6$. The critical temperature being so low, it is much more difficult to liquefy than nitrous oxide.

Nitrogen Sesquioxide or Nitrogen Trioxide, N_2O_3. — Nitrogen sesquioxide is obtained by the action of arsenic trioxide, As_2O_3, upon

nitric acid. Also by the action of nitric oxide upon nitrogen peroxide, the temperature not being above $-21°$: —

$$NO + NO_2 = N_2O_3.$$

Further, it is obtained by the action of a strong acid, like sulphuric, upon nitrites: —

$$2\,NaNO_2 + H_2SO_4 = Na_2SO_4 + H_2O + N_2O_3.$$

It is, therefore, sometimes called nitrous anhydride, since it is nitrous acid minus water; and, by the addition of an alkali, it forms nitrites. Nitrogen sesquioxide is stable only at low temperatures. Above $-20°$, or $-15°$, it begins to decompose into nitric oxide and nitrogen dioxide: —

$$N_2O_3 = NO_2 + NO.$$

At very low temperatures it passes over into a deep-blue liquid.

Nitrogen Dioxide or Nitrogen Peroxide, NO_2. — Nitrogen dioxide is conveniently formed by heating dry lead nitrate: —

$$2\,Pb(NO_3)_2 = 2\,PbO + O_2 + 4\,NO_2.$$

Also by a method which we have recently studied, — the action of oxygen on nitric oxide: —

$$2\,NO + O_2 = 2\,NO_2.$$

It can also be prepared by the direct union of nitrogen with oxygen. When an electric spark is passed through a mixture of these two gases, containing one volume of nitrogen and two volumes of oxygen, they combine to a certain extent, forming nitrogen dioxide: —

$$N_2 + 2\,O_2 = 2\,NO_2.$$

Nitrogen peroxide is a strong oxidizing agent. It is also very poisonous. When treated with cold water it decomposes into nitrous and nitric acids: —

$$2\,NO_2 + H_2O = HNO_2 + HNO_3.$$

When treated with hot water, it yields nitric acid and nitric oxide: —

$$3\,NO_2 + H_2O = NO + 2\,HNO_3.$$

Nitrogen dioxide liquefies at 22°, forming a reddish-brown liquid. As the temperature is lowered the color gradually disappears, until at $-20°$ it passes over into a colorless solid which melts at $-12°$.

The physical properties of the vapor of nitrogen peroxide are

unusually interesting. The vapor-density varies with both the temperature and pressure. The lower the temperature and higher the pressure, the larger the specific gravity of the vapor, and, consequently, the larger the molecular weight calculated from the specific gravity. At comparatively low temperatures (20°), and especially if the pressure is high, the molecular weight is 92, which corresponds to the formula N_2O_4. Above 100°, if the pressure is only a few centimetres, and about 140° at atmospheric pressure, the molecular weight calculated from the vapor-density is 46, corresponding to the formula NO_2.

These changes in the vapor-density are accompanied by corresponding changes in the color of the gas. At low temperatures the vapor is only a little colored, being somewhat yellowish brown. As the temperature is raised the color becomes darker and darker, until finally, at an elevated temperature, it becomes quite dark. When the vapor is cooled again, the original color is restored. We obviously have to deal here with two substances of the composition NO_2, the one, N_2O_4, being a *polymer* of the other. At high temperatures and low pressures only the former exists, having a dark, reddish color. At low temperatures and high pressures we have the compound N_2O_4. As we ordinarily have to deal with the gas, it is a mixture of these two *isomeric substances.*

It is obvious that we have to do here with a condition of equilibrium between the two substances NO_2 and N_2O_4 — a condition which can be changed by varying either the temperature or pressure, and still more by varying both. The higher the temperature and lower the pressure, the more NO_2 is present; the lower the temperature and higher the pressure, the more N_2O_4 is present. If we keep the temperature constant, the pressures of the NO_2 and N_2O_4 in the mixture conform to the equation

$$\frac{p_1^2}{p} = \text{constant},$$

where p_1 is the pressure of the NO_2 and p is the pressure of N_2O_4.

Pure N_2O_4 melts at $-9°$, forming a colorless liquid which freezes to a colorless solid. When warmed it breaks down into NO_2, with its characteristic reddish-brown color.

Nitrogen Pentoxide, N_2O_5. — Nitrogen pentoxide is formed by the action of strong dehydrating agents, like phosphorus pentoxide, upon nitric acid: —

$$2\,HNO_3 + P_2O_5 = (P_2O_5.H_2O) + N_2O_5.$$

Nitrogen pentoxide readily combines with water, forming nitric acid: —

$$N_2O_5 + H_2O = 2\,HNO_3.$$

It is, therefore, the anhydride of nitric acid. It is a powerful oxidizing agent, as would be expected from the large amount of oxygen which it contains, decomposing into nitrogen dioxide and oxygen: —

$$2\,N_2O_5 = 4\,NO_2 + O_2.$$

Nitrogen pentoxide forms colorless crystals, melting at 30°. The liquid boils with partial decomposition at 50°.

Acid Compounds of Nitrogen with Oxygen and Hydrogen. — Nitrogen forms three acids with oxygen and hydrogen; hyponitrous acid, HNO or $H_2N_2O_2$; nitrous acid, HNO_2; and nitric acid, HNO_3. We shall study these somewhat in detail.

Hyponitrous Acid, HNO or $H_2N_2O_2$. — The salts of hyponitrous acid are formed by the careful reduction of nitrates or nitrites by a mild reducing agent, such as sodium amalgam. By the reduction of sodium nitrate, sodium hyponitrite is formed: —

$$2\,NaNO_3 + 4\,H_2O + 8\,NaHg = 8\,NaOH + 8\,Hg + Na_2N_2O_2.$$

The difficultly soluble silver salt is readily prepared from the sodium salt, and the free acid obtained from the silver salt by means of hydrochloric acid dissolved in ether, so as to exclude water: —

$$Ag_2N_2O_2 + 2\,HCl = 2\,AgCl + H_2N_2O_2.$$

It is also prepared by the action of nitrous acid on hydroxylamine: —

$$NH_2OH + HNO_2 = H_2O + H_2N_2O_2.$$

Although hyponitrous acid is a weak acid, shown by the small conductivity of its aqueous solution, it forms both normal and acid salts. The former have the composition $M_2N_2O_2$, the latter, MHN_2O_2.

Hyponitrous acid in aqueous solution decomposes readily into nitrous oxide and water: —

$$H_2N_2O_2 = H_2O + N_2O.$$

Nitrous oxide is, therefore, the anhydride of hyponitrous acid.

Hyponitrous acid forms white crystals, which, when free from water, are very explosive. The molecular weight of hyponitrous acid, as determined by the freezing-point method, corresponds to the double formula $H_2N_2O_2$.

An isomeric acid has been described, having the same composition and same molecular weight as hyponitrous acid, and, therefore,

metameric with it. The difference in the properties of these two substances is supposed to be due to the different arrangement of the atoms in space in the two substances. This kind of isomerism is known as *stereoisomerism*, which apparently plays a more important rôle in organic chemistry than in inorganic.

Nitrous Acid, HNO_2. — The salts of nitrous acid, the nitrites, are obtained by removing oxygen from the nitrates. When a nitrate is carefully heated, it loses oxygen and passes over into a nitrite.

$$2\,NaNO_3 = O_2 + 2\,NaNO_2.$$

If a mild reducing agent, such as metallic lead, is fused with a nitrate, the reduction to nitrite takes place far more easily and completely: —

$$KNO_3 + Pb = PbO + KNO_2.$$

When a nitrite is treated with a strong acid, such as sulphuric, nitrous acid is set free: —

$$2\,KNO_2 + H_2SO_4 = K_2SO_4 + 2\,HNO_2.$$

Nitrous acid can exist only in solution. When an attempt is made to remove the water, the nitrous acid loses water and passes into the anhydride N_2O_3: —

$$2\,HNO_2 = H_2O + N_2O_3.$$

Nitrous acid is an excellent reducing agent, since it readily combines with oxygen, forming nitric acid. When brought in contact with a substance rich in oxygen, like potassium permanganate, it takes oxygen away from the compound, converting it into colorless substances. The destruction of the beautiful purple color takes place very rapidly.

Nitrous acid can also act as an oxidizing agent, giving up some of the oxygen which it already possesses. Thus, it oxidizes hydriodic acid to iodine: —

$$HI + HNO_2 = H_2O + I + NO.$$

Nitric Acid, HNO_3. — This is not only the most important acid of nitrogen, but one of the strongest and most important of all known acids. It was early prepared from nitre, which is potassium nitrate, whence its name. It can be formed by passing electric sparks through a mixture of oxygen and nitrogen, as Cavendish showed. A far better method, however, of preparing nitric acid is by the action of sulphuric acid on some nitrate.

$$H_2SO_4 + 2\,KNO_3 = K_2SO_4 + 2\,HNO_3.$$

A similar reaction takes place when sodium nitrate is treated with sulphuric acid. These methods are used almost exclusively for the preparation of commercial nitric acid, on account of the abundance of these nitrates which occur in nature. Potassium nitrate, known as saltpetre, is formed where organic matter is decomposing in the presence of potassium salts. It occurs in the form of a solid only in arid regions, since, on account of its great solubility, it would pass into solution if it came in contact with any appreciable amount of water. Sodium nitrate occurs in abundance in the arid regions of Chili, and is known as *Chili saltpetre.* When sodium nitrate is treated with sulphuric acid, the first reaction which takes place is: —

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3.$$

If the temperature is raised sufficiently, the acid sulphate acts on more of the nitrate, decomposing it in the sense of the following equation: —

$$NaHSO_4 + NaNO_3 = Na_2SO_4 + HNO_3.$$

In order that this second reaction may take place, such a high temperature must be used that much of the nitric acid is decomposed. Only the first reaction is, therefore, allowed to take place in the preparation of nitric acid.

Chemical Properties of Nitric Acid. — The most characteristic chemical property of nitric acid is its strong oxidizing power. When brought in contact with substances which can take up oxygen, nitric acid readily gives up its oxygen and passes over into lower oxides of nitrogen.

When a metal is treated with nitric acid, the hydrogen ion of the acid gives up its charge to the metal, converting the latter into an ion, while the hydrogen becomes an atom. Thus far nitric acid acts just like the other acids which we have studied. The hydrogen, in the case of nitric acid, however, does not escape, but acts on more nitric acid, reducing it to lower oxides of nitrogen, or to nitrogen itself, or even to ammonia, depending upon conditions. When nitric acid is added to metallic silver it loses one molecule of oxygen, passing over into nitrous acid. When treated with metallic copper, nitric acid is reduced to nitric oxide, NO, as will be remembered; while nitric acid upon zinc is still further reduced, yielding hyponitrous acid, NOH. In the presence of zinc and sulphuric acid nitric acid is reduced to ammonia. The powerful oxidizing action of nitric acid manifests itself towards substances which cannot take the positive electric charge from the hydrogen and become an ion. Thus, phos-

phorus is oxidized by strong nitric acid to phosphorus pentoxide or phosphoric acid, and carbon to carbon dioxide. Metallic tin which does not form a nitrate is oxidized to stannic acid, $Sn(OH)_4$. The salts of nitric acid — the nitrates — are, without exception, very soluble in water. They are excellent oxidizing agents. Nitric acid is still used extensively in the preparation of sulphuric acid. It is also used in the manufacture of certain dyestuffs, and of such explosives as nitroglycerine, nitrocellulose, etc.

Physical Properties of Nitric Acid. — Nitric acid is a liquid, boiling with partial decomposition at 86°. The liquid solidifies at − 47°.

Nitric acid and water are miscible in all proportions. The acid having a specific gravity of 1.1 contains 17.1 per cent of nitric acid; that having a specific gravity of 1.2 contains 32.4 per cent of acid; that having a specific gravity of 1.3 contains 47.5 per cent of acid; that having a specific gravity of 1.4 contains 65.3 per cent of acid, while the pure acid has a specific gravity of 1.53.

All mixtures of nitric acid and water boil higher than pure nitric acid. The relations here are similar to those observed with hydrochloric acid. When any mixture of nitric acid and water is boiled, it tends towards the composition of 68 per cent of the acid. This mixture has a constant boiling-point, which is 120°.5. If the solution of nitric acid in water is more concentrated than 68 per cent, acid will distil over until this concentration is reached. If it is less concentrated than 68 per cent, water will distil over until this concentration of acid remains behind. This composition corresponds approximately to the acid $HNO_3 . 2\,H_2O = N(OH)_5$. That this is a mixture of nitric acid and water and not a definite chemical compound, is proved by the fact that when a different pressure is used the composition of the mixture changes.

Detection of Nitric Acid. — Nitric acid is readily detected by the dark-purple color produced when it is mixed with a concentrated solution of ferrous sulphate, both solutions being warm. The test for nitric acid is made as follows: The nitric acid or the nitrate is treated with a little concentrated sulphuric acid, and warmed until the containing vessel feels quite warm to the hand. Another test-tube is filled about one-third full of crystals of ferrous sulphate, and dissolved in just as little water as possible, the solution being heated until it feels warm to the hand, but not heated to boiling. The solution containing the nitric acid is now added drop by drop to the solution of ferrous sulphate, when the dark color will make its appearance in the form of a ring where the two liquids come in contact.

Dissociation of Nitric Acid and Nitrates. — Nitric acid dissociates in the sense of the following equation: —

$$HNO_3 = \overset{+}{H}, \overset{-}{NO_3}.$$

It is therefore a monobasic acid, and can yield only one series of salts. These are of the general type MNO_3, and dissociate thus: —

$$MNO_3 = \overset{+}{M}, \overset{-}{NO_3}.$$

The conductivity of nitric acid shows that it is one of the very strongest acids known.

v	μ_v (18°)	a
1	299.1	87.3 per cent
20	332.8	97.1 per cent
100	342.1	99.8 per cent
$\mu_\infty = 500$	$= 342.7$	100.0 per cent

Fuming Nitric Acid. — Fuming nitric acid is formed in the preparation of nitric acid from sodium nitrate and sulphuric acid, if the temperature is sufficiently high to cause the acid sodium sulphate to react with more sodium nitrate. It is apparently a solution of nitrogen dioxide in nitric acid.

It is a much more energetic oxidizing agent than ordinary concentrated nitric acid. When warmed in its fumes many organic substances will take fire and burn. When a piece of iron has been dipped in fuming nitric acid for a moment, and is then removed and dipped in ordinary concentrated nitric acid, the latter does not act upon the iron. Iron in this condition is known as in the *passive state*. It was supposed for a long time that the iron became covered with a layer of oxide, which protected it from further action. It is now known that this is not the explanation of the phenomenon, it having been recently shown by the German, Hittorf, that the passive state is purely an electrical phenomenon.

Aqua Regia. — Certain metals, like gold and platinum, do not dissolve in nitric acid, but when treated with a mixture of nitric and hydrochloric acids they dissolve readily. The mixture which is most efficient consists of one part of nitric acid and three parts of hydrochloric acid. This is known as *aqua regia*. The nitric acid in the mixture oxidizes the hydrochloric acid and liberates chlorine. There is probably also formed one or more compounds containing nitrogen, oxygen, and chlorine. These probably have the composi-

tions NOCl and NO_2Cl, and are known, respectively, as *nitrosyl* and *nitryl* chlorides. The action of these various substances is to convert the metals into chlorides, even platinum being transformed into platinic chloride by aqua regia. The name was derived from the fact that this mixture can dissolve gold.

COMPOUNDS OF NITROGEN WITH THE HALOGENS

Compounds of Nitrogen with Chlorine and Bromine. — When chlorine acts upon ammonium chloride, the trichloride of nitrogen, NCl_3, is formed, probably in the sense of the following equation: —

$$3\,Cl_2 + NH_4Cl = 4\,HCl + NCl_3.$$

Nitrogen trichloride is a yellow liquid, which explodes very violently and often with the slightest provocation. The reason for its instability is doubtless closely connected with the endothermic nature of the reaction which produces it. When one nitrogen atom combines with three chlorine atoms, about 42 calories of heat are absorbed. This is set free again when the decomposition of the compound takes place, heating the gases which are formed, and causing them to exert a great pressure. Nitrogen also combines with bromine.

Compounds of Nitrogen with Iodine. — Iodine combines with nitrogen, forming apparently several compounds known as *nitrogen iodides.* When ammonia is treated with iodine at low temperatures, the compound $N_2H_3I_3$ is formed; while at ordinary temperatures we have $N_3H_3I_3$ produced. The compound IN_3 is formed when a solution of iodine in ether is allowed to act on the silver salt of triazoic acid, AgN_3. All of these compounds are characterized by their explosive nature.

COMPOUNDS OF NITROGEN WITH OXYGEN, HYDROGEN, AND SULPHUR

Nitrosyl-sulphuric Acid, $SO_2(OH)NO_2$. — There is one compound of nitrogen with oxygen, hydrogen, and sulphur — nitrosyl-sulphuric acid — which must be considered on account of its importance in the manufacture of sulphuric acid. It will be remembered that this compound is formed by the action of nitrous acid on sulphur dioxide in the presence of the oxygen of the air: —

$$2\,SO_2 + 2\,HNO_2 + O_2 = 2\,SO_2(OH)NO_2.$$

Nitrosyl sulphuric acid crystallizes very frequently in the lead chambers, and is then known as *chamber crystals*. When these come in contact with water-vapor, they decompose in the sense of the following equation: —

$$2\,SO_2(OH)NO_2 + H_2O = 2\,SO_2(OH)_2 + N_2O_3,$$

the products being sulphuric acid and nitrogen sesquioxide.

This compound is also known as *nitrosulphonic acid*.

CHAPTER XVI

THE ATMOSPHERIC AIR AND CERTAIN RARE ELEMENTS OCCURRING IN IT

THE ATMOSPHERIC AIR

It was stated when we were studying nitrogen that the chief source of that element was the atmospheric air. Indeed, it comprises nearly four-fifths of the atmosphere. In addition to nitrogen, we find an abundance of oxygen in the atmosphere. This amounts to nearly one-fifth of the whole. In addition to these two elements we find many other substances, both elementary and compound, in the atmosphere, so that we must study this mixture of gases with some thoroughness.

The meaning of the term *atmospheric air* is well understood. It is that mixture of gases which surrounds our globe, and which is carried along with it as it sweeps through space. The importance of the atmosphere can be seen at once, if we recall that without it the forms of life which are now extant upon the surface of the earth would be at once exterminated.

Composition of the Atmosphere. — In order to determine the exact composition of the atmosphere, we must make a quantitative analysis of it. The oxygen in the air can be determined in several ways. A measured volume of air can be passed over heated copper. The oxygen combines with the copper, forming copper oxide. By weighing the tube containing the copper before the experiment, and weighing the tube containing the copper and copper oxide after the experiment, we know from the gain in weight the weight of the oxygen in a given volume of air. Knowing the weight of a litre of oxygen or of a litre of air, we can calculate at once the percentage of oxygen in the atmospheric air.

Again, the oxygen can be removed from the air by inserting a piece of phosphorus. This will combine with the oxygen and form phosphoric acid. By measuring the original volume of the air, and the volume after all the oxygen has been removed, we have the percentage of oxygen by volume in the atmospheric air.

A third method of determining the amount of oxygen in the air, is to mix with a known volume of air a given volume of hydrogen, and explode the mixture. All the oxygen will combine with the hydrogen and form water, which, at the temperature of the experiment, will be precipitated in the liquid form. From the contraction in volume after the explosion, the amount of oxygen present can be calculated. This last method is known as the *eudiometric method.* Results by the different methods show that the oxygen in the air is about 20.8 per cent by volume, and 23.0 per cent by weight.

The question arises, Does the amount of oxygen present remain constant, or does it vary from place to place or from time to time? While slight variations have been detected, pure air from different parts of the globe, and in different altitudes, varies but slightly in composition.

The remainder of the atmospheric air is nearly all *nitrogen*, a number of other substances occurring in it in very small quantities. There are traces of *carbon dioxide* in the air. The amount can be determined by passing the air through a solution of barium hydroxide, and weighing the amount of barium carbonate precipitated.

The small quantity of *ammonia* in the air can be determined by passing a given volume of air through a solution of a standard acid, and determining how much of the acid is neutralized.

The air under all conditions contains water-vapor. The amount, however, varies greatly from time to time and from place to place. In certain regions far removed from the sea, and over desert land, the amount of water-vapor in the air is comparatively small. Over regions which are close to large bodies of water, the amount of water-vapor in the atmosphere may be quite considerable. To determine the amount of *water-vapor* in the atmosphere, it is only necessary to pass a measured volume of air over some good drying agent, such as phosphorus pentoxide, and determine the increase in the weight of the pentoxide.

Other substances may occur in the atmosphere in very minute quantities, such as ozone, hydrogen dioxide, oxides of nitrogen, and the like, but the quantities are so small that they can, for all practical purposes, be disregarded.

In addition to the constituents already named, there are a number of rare elements which occur in the air in very small quantities. These are the newly discovered elements, argon, helium, neon, krypton, and xenon. These elements we shall consider briefly a little later.

Is the Air a Mixture or a Compound? — The question naturally arises, Is the atmospheric air a chemical compound or a mechanical mixture? The fact that it has so nearly the same composition the world over, would argue in favor of the oxygen and nitrogen being in combination, forming a definite compound. This line of argument, however, is by no means conclusive, since we might easily have the two gases mixed in essentially the same proportion in all regions. Gases diffuse so rapidly that if there was any appreciable difference in composition, it would soon become equalized by diffusion from the region of greater to the region of less concentration. There is, however, direct evidence which shows that the air is simply a mechanical mixture of oxygen and nitrogen, and not a chemical compound.

When air is shaken with water, the part which dissolves has a very different composition from ordinary air. The latter contains in round numbers four parts of nitrogen to one of oxygen, while air which has been dissolved in water contains only 1.9 parts of nitrogen to one of oxygen. This is due to the fact that oxygen is much more readily soluble in water than nitrogen. If air is a compound of oxygen and nitrogen, the compound would dissolve as such, and the air which would be dissolved by water would have the same composition as ordinary air.

Again, chemical union is always accompanied, as we express it, by thermal change. Oxygen and nitrogen mix in the proportion to form air without any thermal change, and air is, therefore, not a chemical compound.

Physical Properties of Atmospheric Air. — The specific gravity of air varies slightly, just as the composition changes slightly. Under the average conditions of zero degrees and 760 mm. pressure, one litre of air weighs 1.293 grams. The pressure of the air, however, decreases very rapidly as we rise from the level of the sea, and a litre of air on the top of a high mountain would weigh much less.

The question as to whether the air has an upper limit, or extends indefinitely into space, has been much discussed. From the general law of the apparently unlimited expansion of gases, in terms of which a gas will occupy the entire space placed at its disposal, it would seem that the atmospheric air must extend out indefinitely into space, the density, however, becoming very small at no great distance from the surface of the earth, and decreasing almost to the infinitesimal at a comparative short distance.

Certain work, however, which has been done on the expansion of very dilute gases, shows that when a certain dilution of the gas has

been reached it does not obey the ordinary law of expansion, but its power to expand is greatly diminished. From this it is highly probable that the atmosphere does not extend to an unlimited distance into space, but that there is an upper boundary to the earth's atmosphere, which is perhaps only a few hundred miles or less from the surface of the earth.

Liquid Air. — We have seen that both oxygen and nitrogen can be liquefied, and would expect, therefore, that atmospheric air, which is essentially a mixture of these two gases, could also be liquefied. Such is the fact. The method employed is based on exactly the same principles which were made use of to liquefy oxygen and similar substances. The most economical method consists in compressing the air and removing the heat set free by a stream of cold water. The compressed air is allowed to expand, when its temperature is very much lowered. It is then allowed to cool other compressed air, which, in turn, is allowed to expand, and a still lower temperature is produced. This is continued until a temperature is reached at which the compressed air, when allowed to expand, becomes partly liquefied. In this process the air is allowed to expand through a fine opening known as a *needle valve*, when part of the compressed air is liquefied and the remainder passes off as gas.

Liquid air has a slightly bluish color. When filtered from solid carbon dioxide and ice it is transparent. It boils at $-190°$. As already stated, the liquid nitrogen, having a lower boiling-point than liquid oxygen, boils off more rapidly, and the liquid remaining after liquid air has been allowed to evaporate for a considerable time, is almost pure liquid oxygen.

Since liquid air is now manufactured on a commercial scale, it is possible to use it on the lecture table for experiments at very low temperatures. Indeed, it is by far the best means at our disposal for producing temperatures in the region of $-180°$ to $-190°$. At these temperatures chemical activity is greatly diminished, and many of the properties of many substances are greatly changed. Some ductile metals become quite brittle, and can be easily broken. Flesh becomes brittle, and can be broken like thin glass. Nearly all liquids are converted into solids when immersed in liquid air. Mercury can be frozen in a mould in the form of a hammer sufficiently hard to drive a nail. Alcohol is readily converted into a solid which resembles semi-transparent ice.

In vacuum-jacketed bulbs liquid air can be preserved for quite a time. Its vapor-pressure is, however, so great, that vessels which contain it must be left open.

ARGON, HELIUM, KRYPTON, NEON, XENON

Argon (At. Wt. = 39.9). — These five elements have all been discovered in the atmospheric air since the summer of 1894. Just before this time Lord Rayleigh had observed that nitrogen obtained from atmospheric air by removing all known constituents was slightly heavier, volume for volume, than nitrogen prepared by heating ammonium nitrite. A litre of nitrogen obtained from the air weighed 1.2572 grams, while a litre of nitrogen from ammonium nitrite, which was known to be chemically pure, weighed 1.2521 grams. No one knew what this meant, but the fact was established beyond question. The most probable explanation seemed to be that the nitrogen from the air contained some impurity which was heavier than nitrogen. Acting upon this line of thought, Rayleigh and Ramsay took up the problem from the chemical side. They determined to remove the oxygen from the air, then the nitrogen and other known constituents, and see if anything remained.

They removed the oxygen from the air by passing it over red-hot copper. The nitrogen was removed from the residue by passing it over red-hot magnesium, the ordinary impurities having been previously removed. There remained a residue which spectrum analysis showed to be a new substance, and which was a little less than one per cent of the atmosphere. Rayleigh and Ramsay were not able to make it combine with any known substance, and from its chemical inactivity called it *argon*. Its vapor-density showed that its molecular weight was 40. When cooled in liquid oxygen and subjected to a pressure of 50 atmospheres, it liquefied at − 187°. It solidified at − 189°.5. All of the facts known point to the elementary nature of argon, and there is not the slightest reason for supposing that it is a compound.

Rayleigh and Ramsay next attempted to determine the number of atoms in the molecule of argon.

Number of Atoms in the Molecule of Argon. — There are several methods for determining the number of atoms in a molecule of a gas. One method is based upon the ratio between the specific heat of the gas at constant-pressure and the specific heat at constant-volume. That it would require more heat-energy to raise the temperature of a given mass of gas, a certain number of degrees at constant-pressure than at constant-volume, is obvious. When the gas is kept at constant-pressure as the temperature is raised, it expands, doing work driving back the atmosphere. If we represent the specific heat at constant-pressure by C_p, and the specific heat at constant-volume by

C_v, when the ratio between these two is 1.66, it has been shown from the kinetic theory of gases that the molecule must be monatomic: —

$$\frac{C_p}{C_v} = 1.66.$$

It would lead us too far to deduce here this relation from the kinetic theory.

The above described method is, on the whole, the one best known in connection with the determination of the number of atoms in a molecule of a gas.

Rayleigh and Ramsay, however, made use of a method which is more convenient, especially when the quantity of substance at disposal is not large. Instead of measuring the two specific heats of argon — at constant-pressure and at constant-volume — they simply measured the velocity of sound in the gas. There is a comparatively simple relation between velocity of sound in a gas and the ratio between the two specific heats of the gas, so that knowing the former, the latter is easily calculated.

Rayleigh and Ramsay did not measure the velocity of sound in the gas directly, but measured the wave-length of sound in the gas by placing some *lycopodium powder* in the glass tube filled with the gas, through which the sound was passing. The lycopodium collects at the points of rest, the nodes, and by measuring the distance between two nodes we have the wave-length of sound in the gas with which the tube is filled. Knowing the wave-length of sound in the gas, and the pitch, we calculate at once the velocity. This is Kundt's method of determining the ratio of C_p to C_v for any gas.

Rayleigh and Ramsay found that the molecule of argon is monatomic. The atomic weight of argon is, therefore, the same as its molecular weight, 40.

Argon has also been found in certain minerals, and in the waters of certain springs.

Helium (At. Wt. = 4), **Neon** (At. Wt. = 20), **Krypton** (At. Wt. = 81.8), **and Xenon** (At. Wt. = 128). — Since the discovery of argon, Ramsay has carried his investigations on the atmospheric air much farther, and has discovered four new substances, all of which appear to be elementary. When air is liquefied two of these escape, being very volatile — helium and neon.

Helium, so called because it had been recognized by means of the spectroscope as occurring in the sun, has also been discovered in the waters of certain springs, and in certain ores of uranium. When a mixture of helium and neon is cooled in liquid hydrogen the neon is

liquefied while the helium remains a gas. Helium does not combine with any known substance, its molecule is monatomic, and its boiling-point somewhat lower than that of hydrogen. It has, then, the lowest boiling-point of any known substance, and has thus far not been liquefied. Its atomic weight, which is identical with its molecular weight, is 4.

Neon has an atomic weight of 20.

Krypton and *xenon* boil higher than air, and were, therefore, found in the residue from the evaporation of a large amount of liquid air. They were separated by the difference in their boiling-points.

The atomic weight of krypton is 81.8, of xenon 128.0.

CHAPTER XVII

PHOSPHORUS (At. Wt. = 31.0)

Occurrence and Preparation. — Phosphorus, discovered by Brandt in 1669, derives its name from the fact that it emits light, or, as we say, is phosphorescent. It does not occur in the free state, but mainly in the form of phosphates, and especially in combination with calcium as the calcium salt. This is the compound of phosphorus which occurs as *apatite*, *phosphorite*, etc., and the great "phosphate beds" in the southern part of the United States are mainly calcium phosphate. Phosphorus also occurs in the bones of animals in the form of the calcium salt, and most of the phosphorus of commerce is made from this source.

Phosphorus is widely distributed through the soil in the form of its salts, and especially of its calcium salt. This comes in part from decomposing rocks which contain phosphates, and also from decomposing animal and vegetable remains. Plants in general take phosphates from the soil and build them up into their own structure. Animals live largely upon vegetables, or upon other animals which live on vegetable food, and thus secure the phosphates which they so much need. The great phosphate beds are supposed to be the remains of animals once living upon the earth.

Phosphorus is of fundamental importance to our highest functions. It occurs in the brain, albumen, etc., and is essential to mental activity.

Phosphorus is prepared from tricalcium phosphate, which has the composition $Ca_3(PO_4)_2$; phosphoric acid, as we shall see, having the composition H_3PO_4. If bones are used as the source of the calcium phosphate, the organic matter is first destroyed by burning.

The tricalcium phosphate is treated with sulphuric acid, when monocalcium phosphate is formed: —

$$Ca_3(PO_4)_2 + 2\,H_2SO_4 = 2\,CaSO_4 + Ca(H_2PO_4)_2.$$

This is then heated, when it passes over into calcium metaphosphate: —

$$Ca(H_2PO_4)_2 = 2\,H_2O + Ca(PO_3)_2.$$

The calcium metaphosphate is then heated with a mixture of silicon dioxide (SiO_2) and powdered charcoal. The following reaction takes place: —

$$Ca(PO_3)_2 + 5\,C + SiO_2 = 5\,CO + CaSiO_3 + 2\,P.$$

In heating the phosphate with carbon and sand the electric furnace is now frequently used. In this case it is not necessary to transform the phosphate into metaphosphate in advance; but the phosphate can be heated at once with carbon and sand, when the reaction expressed by the following equation takes place: —

$$2\,Ca_3(PO_4)_2 + 10\,C + 6\,SiO_2 = 10\,CO + 6\,CaSiO_3 + 4\,P.$$

The phosphorus obtained by the above method is contaminated with various substances. To remove the impurities it is filtered through chamois skin while liquid under water, redistilled, and cast into sticks, in which form it appears on the market.

Properties of Phosphorus. — Phosphorus is a soft solid, with a slightly yellowish tint. In contact with the air it combines readily with the oxygen, forming an oxide of phosphorus. When phosphorus is brought in contact with oxygen a part of the latter is transformed into ozone, as we saw when we were studying ozone.

Phosphorus combines with most of the elements, and with such elements as iodine and bromine with great vigor.

Phosphorus is an extremely poisonous substance, and in working with it precaution must be taken not to inhale its vapors.

While phosphorus when warm has a soft, waxy consistency, when cold it is quite brittle.

Phosphorus melts at 44°.5, forming a yellowish liquid. When heated in an atmosphere free from oxygen it boils at 290°. When heated in contact with oxygen it takes fire at about 50°.

Phosphorus in the form of vapor at low temperatures is composed of molecules of P_4. As the temperature rises these break down into molecules of P_2.

Phosphorus exists in more than one form, there being no less than four allotropic modifications. Ordinary *yellow phosphorus* has already been briefly described. It dissolves readily in carbon disulphide, from which it crystallizes when the solvent is evaporated.

When yellow phosphorus is allowed to stand under water for a long time, exposed to the light, it passes over into a red modification. *Red phosphorus* is easily prepared by heating the yellow phosphorus to 250° in an atmosphere free from oxygen, or to 300° in a vacuum for a few minutes. Red phosphorus is an amorphous powder, and

to the eye resembles in no respect the ordinary variety. The difference between the two is really deep-seated. Red phosphorus is much less active chemically than yellow. When heated to 200° in the air, it does not take fire. When brought in contact with elements and compounds with which yellow phosphorus unites at once, it does not combine with them. Red phosphorus is not soluble in carbon disulphide, and is much less poisonous than the yellow variety.

When red phosphorus is heated to 260° in an atmosphere of carbon dioxide, it passes over quantitatively into the yellow modification.

We have in these two varieties of phosphorus a case somewhat analogous to that met with in the two modifications of oxygen and sulphur. Certain differences are, however, obvious. We saw in the case of sulphur that the real difference between the properties of the two modifications was to be sought for in the different amounts of intrinsic energy present in the two modifications.

Exactly the same relations were discovered in the case of oxygen and ozone. We should, therefore, naturally ask whether there is any similar relation between the two modifications of phosphorus. Do the different modifications contain different amounts of intrinsic energy? This can be answered by burning the different modifications in oxygen, when they yield the same end product, phosphorus pentoxide, P_2O_5. The results of thermochemical measurements show that when yellow phosphorus is transformed into red there are 27,300 calories of heat set free, and this is approximately the thermochemical equivalent of the difference between the intrinsic energies of these two modifications of phosphorus.

When red phosphorus is heated in evacuated tubes to 360°, or mixed with metallic lead and highly heated for a considerable time, another modification of phosphorus appears. The molten lead when allowed to cool is covered with black crystals, and these are also contained within the solidified mass of lead. This form of phosphorus is known as *crystallized, metallic, or black phosphorus.*

Another modification of phosphorus has been prepared by condensing vapors of phosphorus by means of ice-water in an atmosphere of hydrogen. The water becomes covered with a white powder, and this is *white phosphorus.* It has properties quite different from ordinary yellow phosphorus.

It is impossible to say at present whether "black phosphorus" and "white phosphorus" have different amounts of energy in their molecules, and each a different amount from all other modifications, since the necessary thermochemical measurements have not yet been made. From what is known, however, in general concerning the

energy relations which obtain for allotropic modifications of an element, it seems very probable that different amounts of heat would be set free by burning the same amount of these different modifications of phosphorus to the same end product.

A characteristic of ordinary yellow phosphorus is, that it emits light when placed in the dark. This is, undoubtedly, closely connected in some way with the oxidation of the phosphorus, since substances which hinder or prevent the oxidation, reduce or prevent the light-giving power of the element phosphorus.

Compounds of Phosphorus with Hydrogen. — Phosphorus forms three compounds with hydrogen, having, respectively, the following compositions: PH_3, PH_2, and P_2H. At ordinary temperatures the first is a gas, the second a liquid, and the third a solid.

Gaseous hydrogen phosphide, or *phosphine*, is prepared by the action of caustic potash on phosphorus in the presence of water: —

$$3\,KOH + 4\,P + 3\,H_2O = 3\,H_2KPO_2 + PH_3.$$

Phosphine produced by this method always contains a little of the liquid compound PH_2, which renders it spontaneously inflammable. The preparation of phosphine by the above reaction is a very beautiful experiment.

Arrange a flask *A*, as in Fig. 28, and introduce a few grams of caustic potash, dissolved in 15 or 20 cubic centimetres of water. Add

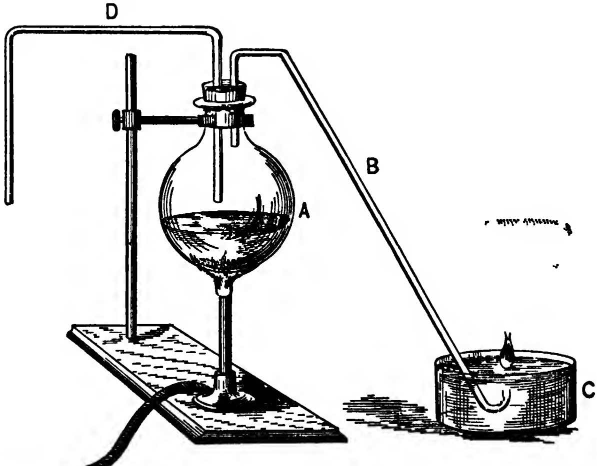


FIG. 28.

a few small fragments of phosphorus. Connect an escape tube as shown at *B*, allowing it to dip beneath the water in the vessel *C*.

This water should be kept warm, in order that the end of the tube may not become stopped up with phosphorus which will distil over from the flask. The flask *A* is connected with a hydrogen generator by means of the glass tube *D*. When the apparatus has become filled with hydrogen from the generator, the solution of caustic potash is gently heated, and phosphine quickly begins to escape. The bubbles, as they come in contact with the air, take fire spontaneously and burn, the phosphorus being oxidized to an oxide of phosphorus, and the hydrogen to water. The products of combustion rise in beautiful rings, which increase in diameter as they ascend, and all together the effect is very beautiful.

Phosphine is obviously the phosphorus analogue of ammonia. Phosphine PH_3, ammonia NH_3. Like ammonia, it can combine with the hydrogen acids of the halogens, the combination taking place by direct addition. The compound with hydriodic acid is formed as follows: —

$$PH_3 + HI = PH_4I,$$

the compound, *phosphonium iodide*, being a white, beautifully crystalline substance, which is not very stable even at ordinary temperatures.

The gas phosphine, which is not spontaneously inflammable, can, however, be burned. It is poisonous, and all work with it should be done under the hood. It is liquefied at 85°, and passes over into a solid at $-132°.5$.

The liquid compound PH_2 or $(PH_2)_2$ is formed along with the gaseous when the latter is made by the method just described. It is the presence of this compound which makes the gas set free in the above experiment spontaneously inflammable. The liquid readily decomposes into the gas PH_3, and the solid P_2H or $(P_2H)_x$.

Compounds of Phosphorus with Oxygen and Hydrogen. — Phosphorus forms a number of compounds with oxygen, indeed four in all. These are phosphorus suboxide, P_4O; phosphorus sesquioxide, P_2O_3; phosphorus tetroxide, P_2O_4; and phosphorus pentoxide, P_2O_5. We have seen that when phosphorus is oxidized on the air, the pentoxide is formed. The other oxides result from the incomplete oxidation of the phosphorus.

Phosphorus suboxide is formed by the action of sodium hydroxide in a mixture of water and alcohol on phosphorus. When the solution is acidified after the action is over, the suboxide is precipitated.

The *tetroxide* is formed by heating the sesquioxide to about 400°. Under these conditions, the sesquioxide breaks down into the tetroxide and phosphorus.

The *sesquioxide of phosphorus*, P_2O_3, is formed by the incomplete oxidation of phosphorus. When phosphorus is burned in a slow current of air, which does not furnish enough oxygen to convert it into the pentoxide, it forms the sesquioxide, which has the composition P_2O_3, but may have the formula P_4O_6. The sesquioxide readily takes up oxygen and passes over into the pentoxide.

Phosphorus pentoxide, P_2O_5, is formed by the oxidation of phosphorus in the presence of an excess of oxygen. It is a beautifully white compound, which has remarkable power to combine with water. Indeed, it is the best drying agent at the disposal of the chemist. Phosphorus pentoxide is the anhydride of an acid. When it combines with the maximum amount of water, it forms phosphoric acid:—

$$P_2O_5 + 3\,H_2O = 2\,H_3PO_4.$$

This brings us to the acids of phosphorus, of which there are several.

The Acids of Phosphorus.—Phosphorus combines with oxygen and hydrogen, forming no less than seven compounds which are acids. These are:—

Phosphoric acid	H_3PO_4
Pyrophosphoric acid	$H_4P_2O_7$
Metaphosphoric acid	HPO_3
Hypophosphoric acid	$H_4P_2O_6$
Phosphorous acid	H_3PO_3
Metaphosphorous acid	HPO_2
Hypophosphorous acid	H_3PO_2

The most important of these, by far, is ordinary phosphoric acid, or orthophosphoric acid.

Orthophosphoric Acid, H_3PO_4.—Orthophosphoric acid is formed, as already stated, by dissolving phosphorus pentoxide in water. It is also formed by the direct oxidation of phosphorus by strong oxidizing agents such as nitric acid. It is in the form of salts of this acid that phosphorus occurs in nature, the calcium salt, Ca_3PO_4, being the compound in which phosphorus occurs in the great phosphate beds. When this salt, which is insoluble in water, is treated with an excess of concentrated sulphuric acid, it is converted into soluble compounds, the compound formed depending upon the amount of sulphuric acid present. When *normal calcium phosphate* is treated with one molecular weight of sulphuric acid the following reaction takes place:—

$$Ca_3(PO_4)_2 + H_2SO_4 = Ca_2H_2(PO_4)_2 + CaSO_4.$$

The salt formed is *secondary calcium phosphate.*

When two equivalents of sulphuric acid are used the salt formed is the *primary calcium phosphate*, and in the sense of the following equation: —

$$Ca_3(PO_4)_2 + 2\,H_2SO_4 = 2\,CaSO_4 + CaH_4(PO_4)_2.$$

When three equivalents of sulphuric acid are used the following reaction takes place: —

$$Ca_3(PO_4)_2 + 3\,H_2SO_4 = 3\,CaSO_4 + 2\,H_3PO_4,$$

giving free orthophosphoric acid.

The above reactions are extensively made use of to render ordinary normal calcium phosphate soluble in water, so that plants can obtain it and take it up into their tissues. These are the fundamental reactions employed in the manufacture of commercial fertilizer either from phosphate rock or from animal bone.

It is obvious from the above that phosphoric acid is a tribasic acid, which forms three series of salts: —

The *tertiary* or *normal phosphates*, having the composition M_3PO_4, where M is a univalent metal; the *secondary* phosphates, having the composition HM_2PO_4; and the *primary* phosphates, having the composition H_2MPO_4.

Dissociation of Phosphoric Acid. — Since phosphoric acid is a tribasic acid, it must dissociate into three hydrogen ions. The complete dissociation of phosphoric acid in the following sense is very difficult to effect: —

$$H_3PO_4 = \overset{+}{H}, \overset{+}{H}, \overset{+}{H}, \overset{\equiv}{PO_4},$$

since phosphoric acid is a comparatively weak acid, as is shown by the following conductivity results: —

v	μ_v (25°)
4	72
32	146
512	297
2048	355

Phosphoric acid dissociates first in the following sense: —

$$H_3PO_4 = \overset{+}{H}, H_2\overset{-}{PO_4}.$$

When more water is added, or when these hydrogen ions have been used up by a base, the second hydrogen begins to split off in the ionic state:—

$$H_2\overset{-}{P}O_4 = \overset{+}{H},\ H\overset{=}{P}O_4.$$

It is not until these hydrogen ions have been used up, or very great dilution has been reached, that the third hydrogen ions begin to split off:—

$$H\overset{=}{P}O_4 = \overset{+}{H},\ \overset{\equiv}{P}O_4.$$

We can now understand why it is quite an easy matter to prepare mono- or primary sodium phosphate by adding sodium hydroxide to phosphoric acid, and also why the secondary salt can be readily prepared. It is, however, not as simple a matter to obtain the tertiary salt in pure condition.

It is a general rule that the salts of weak acids are acted upon by water to a greater or less extent, being broken down into the corresponding acid and base. Take tertiary, or normal sodium phosphate, Na_3PO_4. When this is acted upon by water the following decomposition takes place to some extent:—

$$Na_3PO_4 + H_2O = \overset{+}{Na},\ \overset{+}{Na},\ H\overset{=}{P}O_4 + \overset{+}{Na},\ \overset{-}{O}H.$$

This kind of dissociation is known as *hydrolytic dissociation.* This takes place to a greater or less extent whenever the salt of a weak base with even a strong acid, or even a strong base with a weak acid, or still more when the salt of a weak base with a weak acid is brought into the presence of water. This is the explanation of the alkaline reaction shown by such compounds in water. The hydroxyl ions set free as the result of the combined action of hydrolytic and electrolytic dissociation, give their characteristic alkaline reaction with all indicators sensitive to alkalies. Even the secondary sodium phosphate is hydrolyzed to a slight extent, and shows a feebly alkaline reaction.

Some of the salts already met with undergo hydrolytic dissociation in the presence of water, notably the sulphites. We shall meet many more examples of this kind of dissociation before the subject is ended.

Detection and Determination of Phosphoric Acid.—Phosphoric acid forms a number of insoluble salts with the heavy metals. Some of these have characteristic color. The silver salt, Ag_3PO_4, is yellow. Phosphoric acid is detected when present in very small quantity by adding a nitric acid solution of ammonium molybdate

(a compound which we shall study later), when a complex, yellow precipitate is formed, known as ammonium phospho-molybdate. This compound is soluble in ammonia, and when a mixture of ammonium sulphate and magnesium sulphate is added to the ammoniacal solution, all the phosphoric acid is precipitated quantitatively as the ammonium magnesium salt — NH_4MgPO_4. When this is heated it loses ammonia and water $2\,NH_4MgPO_4 = 2\,NH_3 + H_2O + Mg_2P_2O_7$, and forms the pyrophosphate of magnesium, which is a stable substance and can be easily weighed.

In determining the phosphoric acid in a commercial phosphate, which contains the primary, secondary, and tertiary salt, three determinations are necessary. The primary salt is soluble in water, the secondary salt in an aqueous solution of ammonium citrate, while the tertiary salt is soluble only in acid. The phosphoric acid in each solution is determined as described above. The water soluble plus the citrate soluble constitute the "available" or "soluble" phosphoric acid, while the remainder is "insoluble" phosphoric acid.

Pyrophosphoric Acid, $H_4P_2O_7$. — Pyrophosphoric acid is formed from phosphoric acid by loss of water: —

$$2\,H_3PO_4 = H_2O + H_4P_2O_7.$$

This reaction takes place between 250° and 300°. Salts of this acid are easily obtained by heating secondary phosphates: —

$$2\,HM_2PO_4 = H_2O + M_4P_2O_7.$$

When the lead salt of this acid is treated with hydrogen sulphide, the lead sulphide is precipitated and free pyrophosphoric acid is formed. The presence of this acid is readily detected since its silver salt $Ag_4P_2O_7$ is pure white, while the silver salt of orthophosphoric acid is yellow. Pyrophosphoric acid, since it contains four hydrogen atoms, might yield salts in which one, two, three, and four of these hydrogens were replaced, as we say, by metals. There are, however, only two classes thus far known; those in which two hydrogen atoms are replaced, and those in which four are replaced. Salts in which one and three hydrogens are replaced, if capable of existence, have not thus far been prepared. There is no reason on the face of it why they should not be made.

Metaphosphoric Acid, HPO_3. — Metaphosphoric acid is formed when normal phosphoric acid is heated higher than is necessary to form the pyroacid. When a temperature of about 400° is reached

the second molecule of water passes off from the normal acid, and the metaacid results: —

$$H_3PO_4 = H_2O + HPO_3.$$

It is also formed when phosphorus pentoxide takes up one molecule of water: —

$$P_2O_5 + H_2O = 2\,HPO_3.$$

Salts of this acid are formed when primary phosphates, MH_2PO_4, are heated: —

$$MH_2PO_4 = H_2O + MPO_3.$$

Metaphosphoric acid, on account of its vitreous appearance, is known as *glacial phosphoric acid.* When allowed to stand in contact with water it takes up the water, forming orthophosphoric acid.

It is detected by the fact that its barium salt is a white, insoluble solid.

Hypophosphoric Acid, $H_4P_2O_6$. — Hypophosphoric acid is formed as one of the products of the action of phosphorus on an insufficient supply of air. When the insoluble barium salt is treated with sulphuric acid the free acid is formed.

Phosphorous Acid, H_3PO_3. — Phosphorous acid is formed by the action of phosphorus on moist air. Also by the action of water on a chloride of phosphorus with which we shall soon become familiar, phosphorus trichloride: —

$$PCl_3 + 3\,H_2O = 3\,HCl + H_3PO_3.$$

The acid can be obtained from the solution in the form of crystals which melt at 70°.

Phosphorous acid contains three hydrogen atoms, and would, therefore, be expected to be a tribasic acid. The fact is, it is only dibasic, the salts richest in metal having the composition M_2HPO_3. This is to be explained in terms of its dissociation as follows: The first stage in the dissociation of this substance is represented by the following equation: —

$$H_3PO_3 = \overset{+}{H},\ H_2\overset{-}{P}O_3.$$

The second stage is represented thus: —

$$H_2\overset{-}{P}O_3 = \overset{+}{H},\ H\overset{=}{P}O_3.$$

It is impossible to go farther and split off the last hydrogen atom as an ion. This is not wholly unlike phosphoric acid. We saw

that the first hydrogen atom readily passed into the ionic condition in the presence of water; the second split off much less easily; while the third was converted into an ion only with the greatest difficulty. In the case of phosphorous acid, it is impossible to cause the third hydrogen to pass into the ionic state.

Metaphosphorous Acid, HPO_2.—Metaphosphorous acid is stated to be formed when phosphine undergoes slow oxidation.

Hypophosphorous Acid, H_3PO_2.—Hypophosphorous acid is formed by the action of an alkali on phosphorus. The reaction was referred to when we were dealing with the preparation of phosphine. The free acid is obtained by treating the barium salt with sulphuric acid. Hypophosphorous acid readily takes up oxygen, forming phosphoric acid. It is, therefore, a strong reducing agent.

Hypophosphorous acid contains three hydrogen atoms, and might, therefore, be supposed to be tribasic. The fact is, that it is not even dibasic. It is only monobasic. The salts have the composition MH_2PO_2. The acid must, therefore, dissociate as follows:—

$$H_3PO_2 = \overset{+}{H}, H_2\overset{-}{P}O_2,$$

the ion $H_2\overset{-}{P}O_2$ not being capable of further dissociation.

Strengths of the Acids of Phosphorus.—The relative strengths of a number of the acids of phosphorus can be seen by comparing their conductivities. Take them in the order of increasing amounts of oxygen in the molecule:—

	H_3PO_2 μ_v	H_3PO_3 μ_v	H_3PO_4 μ_v
2	131	121	60
8	194	175	90
32	264	241	146
128	314	298	225
512	339	329	297
1024	346	339	335

There is a rather remarkable relation brought out by the above examples. It is generally true that increase in the amount of oxygen in the molecule increases the strength of the acid. Here, exactly the opposite is true; the more oxygen in the molecule, the weaker the acid, especially in the more concentrated solutions.

COMPOUNDS OF PHOSPHORUS WITH THE HALOGENS

Phosphorus Trichloride, PCl_3. — When chlorine gas is passed over an excess of phosphorus, in an atmosphere free from oxygen, the two combine and form phosphorus trichloride: —

$$2\,P + 3\,Cl_2 = 2\,PCl_3.$$

This compound, when brought in contact with water, decomposes, forming phosphorous acid and hydrochloric acid: —

$$PCl_3 + 3\,H_2O = 3\,HCl + H_3PO_3.$$

Phosphorus trichloride is a colorless liquid boiling at 76°, and passing into the solid form at $-112°$. Phosphorus has the power to take up more chlorine and form phosphorus pentachloride, and to take up oxygen and form phosphorus oxychloride.

Phosphorus Pentachloride, PCl_5. — The pentachloride of phosphorus is formed, as stated above, by the action of chlorine on the trichloride of phosphorus; also by the direct action of an excess of chlorine on phosphorus. Like the trichloride it is readily decomposed by water, forming phosphoric and hydrochloric acids: —

$$PCl_5 + 4\,H_2O = 5\,HCl + H_3PO_4.$$

With a small amount of water it undergoes partial decomposition, yielding the oxychloride of phosphorus and hydrochloric acid: —

$$PCl_5 + H_2O = 2\,HCl + POCl_3.$$

Phosphorus pentachloride is a white solid, which, at an elevated temperature, passes into vapor without melting. The vapor of phosphorus pentachloride is especially interesting in connection with the validity of Avogadro's law. Its vapor-density is less than would correspond to the formula PCl_5. This substance and ammonium chloride were held up as especially prominent examples of compounds which did not obey the law of Avogadro, as we saw when we were considering exceptions to this law.

The explanation which was furnished by experiment was, however, entirely satisfactory. When phosphorus trichloride was volatilized it underwent partial decomposition: —

$$PCl_5 = PCl_3 + Cl_2.$$

The presence of chlorine in the vapor was shown by its green color.

When phosphorus pentachloride is volatilized, however, in the presence of an excess of either of its decomposition products (PCl_3 or Cl_2), its vapor has a density which corresponds to the formula PCl_5; just as when ammonium chloride is volatilized in the presence of an excess of either of its decomposition products (NH_3 or HCl), it gives normal molecular weight.

These are excellent examples of the effect of mass on chemical activity. When the mass of any of the dissociation products is increased, the dissociation is driven back as we say, *i.e.* the constituents remain united or, if once separated, unite again to form the original compound. The law governing the influence of mass has already been taken up.

Phosphorus Oxychloride, $POCl_3$. — Phosphorus oxychloride, a liquid with a very penetrating and nauseating odor, is formed, as we have already seen, by the action of water on the pentachloride of phosphorus. Just as it is the product of the first stage in the decomposition of phosphorus pentachloride with water, so when treated with water it undergoes further decomposition, yielding hydrochloric acid and phosphoric acid: —

$$POCl_3 + 3\,H_2O = 3\,HCl + H_3PO_4.$$

Phosphorus also forms compounds with bromine, iodine, and fluorine.

CHAPTER XVIII

ARSENIC (At. Wt. = 75.0)

Occurrence and Preparation. — An element closely allied chemically to phosphorus is arsenic. That there are marked differences, however, will appear as the following chapter develops.

Arsenic does occur in the free condition. It is generally in combination with the metals, either directly as in the compound with iron, Fe_2As_3, or with sulphur as in *arsenical pyrites*, FeAsS.

Arsenic is generally obtained from its compounds by simply heating them; the arsenic, being volatile, passes off as vapor.

Properties of Arsenic. — Arsenic is a solid at ordinary temperatures, gray in color and very brittle. It combines with oxygen, slowly at ordinary temperatures, but rapidly at elevated temperatures, with evolution of light and heat. In an atmosphere of chlorine it burns readily, forming a chloride of arsenic. Arsenic in the form of vapor is composed of molecules of As_4.

Compound of Arsenic with Hydrogen — Arsine, AsH_3. — Arsenic forms with hydrogen the compound AsH_3, which is analogous to ammonia, NH_3. It is formed by the action of nascent hydrogen on compounds of arsenic. When we have a compound of arsenic in the presence of zinc and an acid, arsine is formed. If the compound is ordinary arsenic trioxide, As_2O_3, this is reduced by nascent hydrogen as follows: —

$$As_2O_3 + 6\,H_2 = 3\,H_2O + 2\,AsH_3.$$

When arsine is heated it is broken down into its elements, arsenic and hydrogen. When arsine is burned and a cold object introduced into the flame, arsenic is deposited upon the object. These reactions are made use of for the detection of arsenic. Marsh's method for detecting arsenic consists in reducing the arsenic compound to arsine and burning the arsine.

The apparatus used is shown in Fig. 29. Into the flask *A* some zinc which is perfectly free from arsenic is introduced. Upon this is poured some pure, dilute, sulphuric acid, which acts upon the zinc, generating hydrogen. The tube *C*, containing calcium chloride, is introduced for the purpose of drying the gas. When the apparatus has become filled with hydrogen, the gas is ignited as it escapes

from the end of the tube *B*. The substance which is supposed to contain arsenic is dissolved in hydrochloric acid, and added to the contents of the flask *A*. If arsenic is present, arsine will be formed and will escape mixed with the hydrogen. If arsine is present, the color of the hydrogen flame will change very perceptibly. The

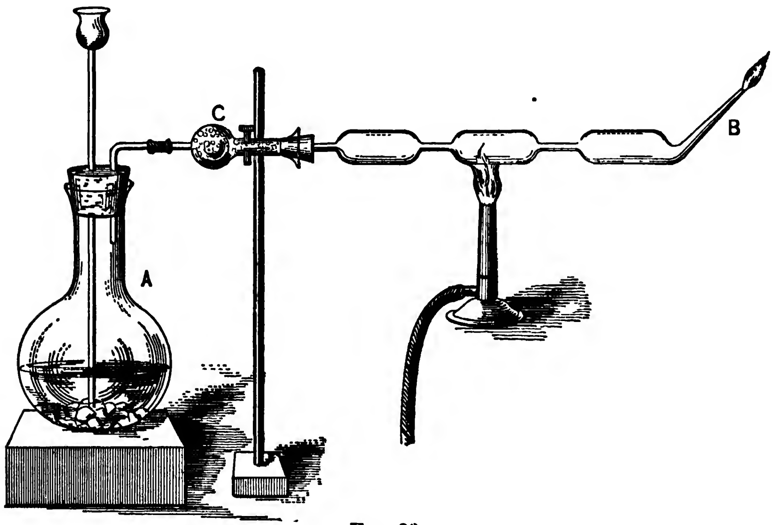


FIG. 29.

almost colorless flame of the hydrogen will become milky-white in color with a greenish-blue tint. If now the tube is heated, the arsine will be decomposed and a mirror of arsenic will be deposited upon the walls of the tube. A cold evaporating dish inserted into the flame will become covered with a layer of arsenic.

In order that this test should be of any value, all the materials used must be perfectly free from arsenic. In testing for arsenic the greatest precaution should be taken to secure this result.

COMPOUNDS OF ARSENIC WITH OXYGEN AND HYDROGEN

Compounds of Arsenic with Oxygen. — Arsenic forms two compounds with oxygen. One of these has the composition As_2O_3, and is known as arsenic trioxide, or arsenious oxide; the other has the composition As_2O_5, and is known as arsenic pentoxide, or arsenic oxide.

Arsenic Trioxide, As_2O_3, is formed when arsenic is oxidized either by burning in the air, or by some strong oxidizing agent such as nitric acid.

Arsenious oxide or arsenic trioxide is a white solid, which passes

gradually into the crystalline condition. Arsenic trioxide crystallizes in more than one form, and thermal changes take place when one form is transformed into another. It, therefore, exists in allotropic modifications. When heated, arsenic passes at once into vapor without melting. If, however, it is subjected to a higher pressure it can be melted. In this case, as in so many others, the melting-point is higher than the boiling-point under atmospheric pressure.

The vapor-density of arsenic trioxide varies with the temperature. Below 800° the vapor-density corresponds to the double formula, As_4O_6. As the vapor becomes heated higher and higher the vapor-density becomes less and less, until at from 1700° to 1800° the vapor-density corresponds to the formula As_2O_3. This is another substance whose molecule in the form of vapor is more complex at lower temperatures, and *dissociates* into simpler molecules as the temperature rises. The molecular weight of arsenic trioxide in nitro-benzene has been determined by the boiling-point method, and found to correspond to the double formula, As_4O_6.

Arsenic trioxide is in a sense the anhydride of arsenious acid, just as phosphorus trioxide is the anhydride of phosphorous acid. Arsenic trioxide is, however, only slightly soluble in water.

Arsenic trioxide is the form in which arsenic comes most frequently on the market. It is known as *white arsenic*, and is very poisonous. The best antidote for arsenic poisoning is a mixture of magnesia and ferric hydroxide. The arsenic is precipitated by this mixture probably in the form of ferric and magnesium arsenite, which is only slightly soluble.

Arsenic Pentoxide, As_2O_5. — Arsenic pentoxide cannot be formed like phosphorus pentoxide by burning the element in oxygen. Indeed, if arsenic pentoxide is heated to a fairly high temperature, it breaks down into arsenic trioxide and oxygen. It is prepared by removing water from arsenic acid, and is, therefore, the anhydride of this acid. It is also prepared by heating arsenic trioxide with some strong oxidizing agent such as nitric acid.

Arsenious Acid, H_3AsO_3. — This acid is not known in the free condition. There are, however, three classes of salts known, depending upon whether one, two, or three of the hydrogen ions have given their electrical charges to the metal atoms which have entered the compound. This acid can apparently lose the elements of water and form *metaarsenious acid:* —

$$H_3AsO_3 = H_2O + HAsO_2.$$

At least salts of this acid are known.

Arsenic Acid, H_3AsO_4. — When ordinary white arsenic, or arsenic trioxide, is heated with some strong oxidizing agent such as nitric acid or aqua regia in the presence of water, it is oxidized to arsenic acid. The reaction consists in the direct addition of oxygen and water: —

$$As_2O_3 + O_2 + 3\,H_2O = 2\,H_3AsO_4.$$

The acid is known in solution as a syrupy liquid, and in the solid form as white needles. Like phosphoric acid it forms three series of salts, primary, secondary, and tertiary. It must, therefore, dissociate in the three stages: —

$$H_3AsO_4 = \overset{+}{H},\ H_2\overset{-}{As}O_4,$$
$$H_2\overset{-}{As}O_4 = \overset{+}{H},\ H\overset{=}{As}O_4,$$
$$H\overset{=}{As}O_4 = \overset{+}{H},\ \overset{\equiv}{AsO_4}.$$

Arsenic acid, like phosphoric acid, loses water in stages forming the pyro-, and meta- acids. When two molecules of the acid lose one molecule of water the *pyro-* acid is formed: —

$$2\,H_3AsO_4 = H_2O + H_4As_2O_7.$$

When one molecule of the acid loses one molecule of water the *metaarsenic* acid results: —

$$H_3AsO_4 = H_2O + HAsO_3.$$

When primary salts of arsenic acid are heated the following reaction takes place: —

$$H_2MAsO_4 = H_2O + MAsO_3.$$

When secondary salts are heated they yield *pyroarsenates:* —

$$2\,HM_2AsO_4 = H_2O + M_2As_2O_7.$$

Here again the resemblance between arsenic and phosphorus appears.

Compounds of Arsenic with the Halogens. — Arsenic forms a number of compounds with the halogens. The best known is the *trichloride,* formed by the action of hydrochloric acid on arsenic trioxide,

$$As_2O_3 + 6\,HCl = 3\,H_2O + 2\,AsCl_3,$$

or by the direct union of arsenic and chlorine, which readily takes place. Arsenic trichloride is decomposed by water as follows: —

$$AsCl_3 + 3\,H_2O = 3\,HCl + H_3AsO_3.$$

This reaction seems to be exactly the reverse of the above. When arsenic trioxide is heated with hydrochloric acid, arsenic trichloride and water are formed. On the other hand, when the trichloride is heated with water, hydrochloric acid and arsenious acid are formed.

Here we have again a good example of the effect of mass on chemical activity. In order to have the first reaction take place, a large amount of hydrochloric acid must be used. In order to effect the second reaction a large amount of water must be present. The effect of mass here is such as to condition the way in which the reaction proceeds.

Compounds of Arsenic with Sulphur.—Arsenic forms no less than three compounds with sulphur.

Arsenic disulphide As_2S_2 occurs in nature as the mineral *realgar.* It can also be prepared by fusing together the two elements in equivalent quantities.

Arsenic trisulphide As_2S_3 occurs in nature as the mineral *orpiment.* It is formed by the action of hydrogen sulphide on arsenious acid:—

$$2\,H_3AsO_3 + 3\,H_2S = 6\,H_2O + As_2S_3.$$

It can be formed also by fusing two equivalents of arsenic with three of sulphur. This compound, on account of its fine yellow color, was formerly used as a pigment.

Arsenic pentasulphide As_2S_5 is formed when hydrogen sulphide is conducted into a cold, hydrochloric acid solution of arsenic acid:—

$$2\,H_3AsO_4 + 5\,H_2S = As_2S_5 + 8\,H_2O.$$

It is also obtained by fusing arsenic with an excess of sulphur, when the two combine and form the pentasulphide:—

$$2\,As + 5\,S = As_2S_5.$$

The excess of sulphur can be dissolved in carbon disulphide and removed. On account of its insolubility in water, it is the form in which arsenic is usually precipitated and weighed in quantitative analysis.

Sulpho-salts of Arsenic.—Arsenic forms with sulphur and the alkali metals, salts of acids having the composition H_3AsS_3 and H_3AsS_4. These acids are the sulphur analogues of arsenious acid H_3AsO_3 and arsenic acid H_3AsO_4. The sulpho-acids or thio-acids are themselves not known, but certain salts are well-characterized substances.

Thus, when arsenic trisulphide is treated with sodium, potassium, or ammonium sulphide, the two combine as follows, M representing the alkali metal: —

$$3\,M_2S + As_2S_3 = 2\,M_3AsS_3.$$

This is obviously the salt of *sulpharsenious* or *thioarsenious acid,* and is known as a sulpharsenite or thioarsenite.

Similarly, when the pentasulphide of arsenic is treated with an alkaline sulphide, the two combine: —

$$3\,M_2S + As_2S_5 = 2\,M_3AsS_4.$$

There is formed the salt of *sulpharsenic acid* or *thioarsenic acid,* and this is known as a sulpharsenate or thioarsenate.

The analogy between the sulphur acids of arsenic and the oxygen acids can be carried still farther. Just as we have salts of sulphur acids corresponding to arsenious and arsenic acids, so, also, we have salts of a sulphur acid corresponding to metaarsenic acid, $HAsO_3$. When the trisulphide of arsenic is treated with a polysulphide of an alkali metal, we have: —

$$M_2S_3 + As_2S_3 = 2\,MAsS_3,$$

which is a sulphometaarsenate.

The above compounds of arsenic with sulphur and the alkali metals, are of fundamental importance in separating arsenic from other elements. Arsenic is precipitated as the sulphide, along with a number of other sulphides, by means of hydrogen sulphide. The sulphide of arsenic is soluble in the polysulphide of ammonium, forming sulpho-salts; and is thus separated from most other substances.

CHAPTER XIX

ANTIMONY (At. Wt. = 120.2)

Occurrence and Preparation. — Another element which presents many chemical analogies to phosphorus and arsenic is antimony. Antimony occurs in nature chiefly as the trisulphide, Sb_2S_3, which is the well-known mineral *stibnite*. It also occurs in combination with arsenic and also with oxygen.

Antimony is prepared from stibnite by roasting out the sulphur. The sulphide is heated in the air, when the sulphur is converted into the dioxide, and the antimony into the trioxide or sesquioxide, Sb_2O_3. The oxide is then reduced with carbon: —

$$2\,Sb_2O_3 + 3\,C = 3\,CO_2 + 4\,Sb.$$

Antimony sulphide is sometimes heated with iron, when the iron combines with the sulphur forming iron sulphide, and antimony is set free.

Properties of Antimony. — Antimony is a bluish-white solid with metallic lustre. It melts at 630° and boils at 1450°. It combines with oxygen at elevated temperatures, but not at ordinary temperatures. Like arsenic it combines readily with chlorine at ordinary temperatures. When a piece of antimony highly heated in the air is thrown upon white paper, it continues to run about over the surface of the paper, leaving tracings which are often very beautiful.

The vapor-density of antimony decreases with rise in temperature. At the boiling temperature the vapor of antimony probably consists of molecules of Sb_4, which break down into simpler molecules as the temperature rises.

Compound of Antimony with Hydrogen — Stibine, SbH_3. — Antimony forms with hydrogen the compound SbH_3, which is analogous to the compounds of hydrogen with nitrogen, phosphorus, and arsenic.

NH_3	ammonia
PH_3	phosphine
AsH_3	arsine
SbH_3	stibine

Of these substances only ammonia has pronounced basic properties, but, as we have seen, this is not a very strong base. Stibine is formed in a manner strictly analogous to arsine, by the reduction of antimony compounds by nascent hydrogen. When a solution of an antimony compound in hydrochloric acid is introduced into a flask in which hydrogen is being generated, the antimony is reduced to stibine. Stibine like arsine is unstable at an elevated temperature. When heated to 150° it breaks down into antimony and hydrogen. When ignited it burns with a characteristic pale, greenish flame, which deposits a mirror of antimony on a cold object introduced into it. These facts are utilized for detecting antimony by the method of Marsh. The procedure for detecting antimony is exactly analogous to that employed for detecting arsenic, and the results are very similar if antimony or if arsenic is present. If either is present the metal-like mirror appears when the tube is heated, and the dark spot forms on the cold porcelain when it is held in the flame. The question arises, How can we tell whether we are dealing with arsenic or with antimony, or with both? There are certain differences between the two deposits which enable us to distinguish the one from the other. The deposit of arsenic is very volatile, readily moving along the tube when the flame is placed beneath it. Antimony, on the other hand, is much less volatile, forming little globules when heated. The arsenic mirror is soluble in sodium hypochlorite, while the antimony is not. When the mirror is treated with hydrogen sulphide, if it is arsenic it is converted into the yellow sulphide of arsenic; if antimony, into the red sulphide of antimony.

COMPOUNDS OF ANTIMONY WITH OXYGEN AND HYDROGEN

With oxygen alone antimony forms three compounds: antimony trioxide — Sb_2O_3, antimony tetroxide — Sb_2O_4, and antimony pentoxide — Sb_2O_5.

Oxides of Antimony. — The oxide of antimony containing the least amount of oxygen is the *trioxide* or *sesquioxide*, Sb_2O_3. It occurs in nature as *senarmontite*, and is readily prepared by oxidizing antimony either with some strong oxidizing agent such as nitric acid, or by burning antimony in the air. In the latter case there is some of the higher oxide, SbO_2, formed along with the trioxide.

When antimony trioxide is treated with strong acids it forms salts, and, therefore, has basic properties. When these salts are

treated with a large volume of water they decompose readily, yielding the free acid and the compound $Sb(OH)_3$. This hydroxide loses water easily and passes over into the trioxide:—

$$2\,Sb(OH)_3 = 3\,H_2O + Sb_2O_3.$$

It may, however, lose only one molecule of water and form meta-antimonious acid:—

$$Sb(OH)_3 = H_2O + HSbO_2.$$

Salts of this acid with certain metals are known, having the composition $MSbO_2$.

The compound $HSbO_2$, which can also be regarded as $SbO.OH$, can form salts with strong acids. The group SbO seems to act as a unit, and is known as the antimonyl group. The best-known antimonyl compound is the double tartrate of potassium and antimony. This is known as *tartar emetic*. It has the composition $SbOK.C_4H_4O_6$.

Potassium antimonyl tartrate is an antimony compound which is readily soluble in water.

Antimony trioxide is a yellow powder which boils at 1560°. At this temperature the vapor-density has been determined and corresponds to the formula Sb_4O_6.

The *tetroxide of antimony*, Sb_2O_4, is formed, as we have seen, by burning antimony in the air, especially at a high temperature. It is also formed by highly heating the trioxide in the presence of air. Like the trioxide, the tetroxide has both acid and basic properties, depending upon the conditions. Towards strong acids it acts like a weak base, while towards strong bases it acts, when combined with water, like an acid. We have salts corresponding to the general formula $M_2Sb_2O_5$. These are obviously salts of the acid $H_2Sb_2O_5$, which is formed by the union of the compound Sb_2O_4 with a molecule of water:—

$$Sb_2O_4 + H_2O = H_2Sb_2O_5.$$

It is interesting to ask how a compound can be both acidic and basic, depending upon the conditions. How does such a compound dissociate? In the presence of a strong acid, where there are many hydrogen ions in the solution, the compound dissociates yielding hydroxyl ions, which combine with the hydrogen ions of the acid, forming water. If the compound is brought into the presence of a strong base where there are many hydroxyl ions, it dissociates yielding hydrogen ions, which combine with the hydroxyl ions forming water. We can thus see how the same compound can be acidic or

basic, depending upon the conditions. We shall meet other and better examples of this same kind of action.

Antimony pentoxide, Sb_2O_5, is obtained either by heating antimony with a strong oxidizing agent like nitric acid, or by carefully removing the water by heat from antimonic acid. The compound, we shall learn, has the formula H_3SbO_4, and when heated, —

$$2\,H_3SbO_4 = 3\,H_2O + Sb_2O_5.$$

When antimony pentoxide is heated it loses oxygen and passes over into the tetroxide.

Acids of Antimony. — Antimony combines with hydrogen and oxygen, forming several compounds which are acids, but these are not so numerous as in the cases of phosphorus and arsenic. Indeed, the compound $Sb(OH)_3$ has distinctly basic properties towards strong acids, as we have seen, and *metaantimonious acid* itself, SbOOH, may act basic as in potassium antimonyl tartrate. Although the basic-forming property begins to manifest itself in antimony, yet it forms certain well-defined acids. The best known of these is *antimonic acid*, having the composition H_3SbO_4. This is formed by the action of strong oxidizing agents such as nitric acid or aqua regia, on antimony. It is also formed when the pentachloride of antimony is treated with water, which is analogous to the formation of phosphoric acid from phosphorus pentachloride: —

$$SbCl_5 + 4\,H_2O = 5\,HCl + H_3SbO_4.$$

When antimonic acid is heated to 175°, it loses water, passing first into *metaantimonic acid:* —

$$H_3SbO_4 = H_2O + HSbO_3.$$

Salts of *pyroantimonic acid* have been prepared. We can regard this acid as being formed from antimonic acid, in the same way as pyrophosphoric acid is formed from phosphoric acid by loss of water: —

$$2\,H_3SbO_4 = H_2O + H_4Sb_2O_7.$$

The sodium salt of this acid has the composition, $Na_2H_2Sb_2O_7$. A potassium salt is known having the composition, $K_4Sb_2O_7$, but this readily breaks down, in the presence of water, into potassium hydroxide and the compound $K_2H_2Sb_2O_7$. The acid $H_4Sb_2O_7$ must, therefore, dissociate into $\overset{+}{H}$, $\overset{+}{H}$, $H_2\overset{=}{Sb_2O_7}$, and it is only under extreme circumstances that more than two hydrogen atoms separate as ions.

Compounds of Antimony with the Halogens. — Antimony forms two compounds with chlorine — the trichloride and the penta-

chloride. *Antimony trichloride,* $SbCl_3$, is formed by the action of a mixture of hydrochloric and nitric acids on antimony; also by the action of chlorine on an excess of antimony at an elevated temperature. It is a soft solid, which, on account of its consistency, is known as *antimony butter.*

When antimony trichloride is treated with water, oxychlorides are formed, which are, however, decomposed by an excess of boiling water, losing all their chlorine and passing over into antimony trioxide.

Antimony pentachloride, $SbCl_5$, is formed by the action of an excess of chlorine on antimony at an elevated temperature. The antimony burns in the chlorine, with an evolution of light and heat. It is also formed by the action of chlorine on antimony trichloride. Antimony pentachloride is a liquid at ordinary temperatures, boiling at 140° and freezing at − 6°. At its boiling-point the vapor is only slightly decomposed, thus differing from the pentachloride of phosphorus. When antimony chloride is treated with small amounts of water it combines with the water, forming definite hydrates; when boiled with an excess of water it decomposes, forming antimonic acid. Antimony combines with bromine, forming the *tribromide,* $SbBr_3$; with iodine, forming a *triodide* and possibly a *pentaiodide,* and with fluorine, forming a *tri-* and a *pentafluoride.*

Compounds of Antimony with Sulphur.—Antimony forms two compounds with sulphur—the trisulphide and the pentasulphide. *Antimony trisulphide,* Sb_2S_3, occurs in nature as *antimony blende.* It is formed by the action of hydrogen sulphide on a solution of an antimony salt, in which the antimony is in the trivalent condition. When hydrogen sulphide is conducted into a solution of antimony trichloride, in the presence of a little hydrochloric acid, the following reaction takes place:—

$$2\,SbCl_3 + 3\,H_2S = Sb_2S_3 + 6\,HCl.$$

Antimony trisulphide thus prepared has a dark-red color, with a slightly brownish tint. It is soluble in concentrated hydrochloric acid, and also in solutions of alkaline sulphides, forming salts of sulpho-acids of antimony, which will be considered a little later.

Antimony pentasulphides, Sb_2S_5, is formed by the action of hydrogen sulphide on an antimony salt, in which the antimony is pentavalent. When antimony pentasulphide in solution in the presence of tartaric acid is treated with hydrogen sulphide, the following reaction takes place:—

$$2\,SbCl_5 + 5\,H_2S = 10\,HCl + Sb_2S_5.$$

It is also formed when hydrogen sulphide is passed into an acidified solution of antimonic acid: —

$$2\,H_3SbO_4 + 5\,H_2S = 8\,H_2O + Sb_2S_5.$$

Antimony pentasulphide is an orange-red powder, not soluble in dilute, but dissolves in concentrated acids. It dissolves when treated with the sulphides or polysulphides of the alkalies, forming sulpho-salts of antimony, which will now be considered.

Compounds of Antimony with Sulphur and the Metals. — We have seen that arsenic combines with sulphur and the metals, forming salts of sulpho-acids of arsenic. In an analogous manner, antimony forms salts of sulpho-acids. When antimony trisulphide is treated with the sulphide of an alkali metal, such as potassium sulphide, ammonium sulphide, or polysulphide, the antimony trisulphide dissolves, forming a salt of a sulpho-acid, $MSbS_2$, which is a *metasulphantimonite.* Salts of *sulphantimonious* acid, H_3SbS_3, are also known.

When antimony pentasulphide is dissolved in an alkaline sulphide, salts of sulphantimonic acid are formed: —

$$Sb_2S_5 + 3\,Na_2S = 2\,Na_3SbS_4.$$

This compound, which contains nine molecules of water, is known as *Schlippe's salt.* It is also formed by the action of caustic soda on antimony trisulphide and sulphur.

These sulphur acids are the strict analogues of the oxygen acids, containing sulphur in the place of oxygen. When the sodium salt of sulphantimonic acid dissociates, the ions are: —

$$Na_3SbS_4 = \overset{+}{Na}, \overset{+}{Na}, \overset{+}{Na}, \overset{\equiv}{Sb}S_4.$$

The ion $\overset{\equiv}{Sb}S_4$ cannot be regarded as very stable, since when the above salt is treated with an acid, which is the same as to add a large number of hydrogen ions, the acid H_3SbS_4 is not formed, but this breaks down into hydrogen sulphide and antimony pentasulphide.

Hard Lead. — When antimony is fused with lead, the alloy is much harder than lead, and is known as hard lead. Another alloy of antimony and lead is known as type-metal.

CHAPTER XX

BISMUTH (At. Wt. = 208.5)

The last member of the nitrogen, phosphorus, arsenic, antimony family of group V in the Periodic System is bismuth. We have seen that as the atomic weight increases, the elements become less acidic, and the basic properties begin to manifest themselves. This condition, which has already appeared in antimony, is intensified in the element which we are now about to study — bismuth.

Occurrence and Properties. — Bismuth occurs mainly in the free condition, but also combined with sulphur as the trisulphide, Bi_2S_3. Bismuth is obtained from the sulphide by burning out the sulphur with oxygen, when it is transformed into the oxide. The oxide is then reduced by carbon, yielding the element.

Bismuth is a crystallized solid. It forms crystals which are *isomorphous* with arsenic and antimony, *i.e.* the crystals have the same form, and the two substances can crystallize together. Bismuth combines directly with oxygen at an elevated temperature, forming the trioxide. Like the other members of this group, it combines directly with the halogens. Bismuth melts at 264°, and it boils in an atmosphere of hydrogen at about 1600°.

The metallic nature of bismuth begins to manifest itself in its behavior towards the electric current. It shows very marked conductivity.

Some of the most important substances containing bismuth are certain of its alloys with other metals. These have the remarkable property that they fuse far below the melting-point of the lowest-melting constituent. The well-known *Rose's fusible metal* consists of one part of lead, one part of tin, and two parts of bismuth. It fuses at 93°.8. Another alloy of the same metal, consisting of five parts of lead, three parts of tin, and eight parts of bismuth, fuses at 94°.5. There is an alloy of bismuth still more remarkable than the above, in that it fuses at 60°.5, and is known as *Wood's metal*. This contains two parts of lead, one part of tin, four parts of bismuth, and one part of cadmium. It is the lowest-melting alloy of these substances, and is, therefore, known as their *eutectic alloy* —

a eutectic alloy of any two or more metals being the lowest-melting alloy of those substances. These alloys are used in scientific investigations where a low-melting metal is needed. When Wood's metal is heated in a test-tube with water it melts long before the water boils.

Compounds of Bismuth with Oxygen and Hydrogen. — While bismuth forms four compounds with oxygen, bismuth oxide BiO, bismuth sesquioxide Bi_2O_3, bismuth dioxide BiO_2, and bismuth pentoxide Bi_2O_5, the only compound of importance is the sesquioxide. It is formed when bismuth burns in the air. It combines readily with acids, forming water and the corresponding salt, and is, therefore, a base.

The corresponding hydroxide, $Bi(OH)_3$, has decidedly basic properties. It combines with acids forming salts of the general type BiR_3, where R is the anion of a monobasic acid. Thus, with nitric acid bismuth hydroxide forms the salt $Bi(NO_3)_3$. The compound $Bi(OH)_3$ is, therefore, a triacid base, dissociating as follows: —

$$Bi(OH)_3 = \overset{+++}{Bi}, \ \overset{-}{OH}, \ \overset{-}{OH}, \ \overset{-}{OH}.$$

The compound $BiO.OH$ derived from $Bi(OH)_3$ by loss of water — $Bi(OH)_3 = H_2O + BiO.OH$ — is also basic. Thus, with nitric acid this base forms the compound $BiO.NO_3$, and possibly also the compound $Bi(NO_3)_3$. The group BiO is known as *bismuthyl*, and its salts as bismuthyl salts, or basic bismuth salts.

When bismuth nitrate is treated with water it passes over into a basic nitrate or subnitrate of bismuth. Bismuth hydroxide has slightly acid properties when in the presence of a strong base like potassium hydroxide. The compound formed is, however, very unstable.

Bismuth Chloride, $BiCl_3$. — That bismuth can form a trichloride we would expect from the triacid nature of its hydroxide. It is, however, not formed by treating bismuth hydroxide with aqueous hydrochloric acid, since the water present would decompose it and give a basic salt.

It is formed by the action of chlorine on bismuth and has the composition $BiCl_3$. When this is treated with water it passes over into the oxychloride $BiOCl$, which is really the chloride of the group bismuthyl — BiO.

Bismuth Sulphide, Bi_2S_3. — This compound occurs in nature as *bismuth blende*. It is readily made in the laboratory by treating a solution of a bismuth salt with hydrogen sulphide: —

$$2\,Bi(NO_3)_3 + 3\,H_2S = Bi_2S_3 + 6\,HNO_3.$$

It is a black substance, and is the form in which bismuth is usually precipitated in qualitative analysis. The sulphide of bismuth is practically insoluble in an aqueous solution of an alkaline sulphide, and is thus separated from arsenic and antimony.

Bismuth sulphide is insoluble in dilute acids, but dissolves in hot, concentrated, hydrochloric acid.

CHAPTER XXI

VANADIUM, COLUMBIUM, NEODYMIUM, PRASEODYMIUM, TANTALUM

The remaining members of this natural group of elements are vanadium, columbium, neodymium, praseodymium, and tantalum. These are all very rare substances and will, therefore, be considered very briefly.

Vanadium (At. Wt. = 51.2). — Vanadium occurs in nature chiefly as vanadates. These are salts of the acid H_3VO_4. Vanadium also forms a metavanadic acid HVO_3. Vanadium combines with oxygen forming the pentoxide, V_2O_5, which has weakly basic properties. It also forms a trioxide or sesquioxide V_2O_3. Vanadium forms the chlorides VCl_4., VCl_3, and VCl_2. It also forms the oxychloride $VOCl_3$. Vanadium combines directly with nitrogen at an elevated temperature, forming the compound VN. Indeed, vanadium is one of the few elements which burn in nitrogen.

Columbium (At. Wt. = 94.0). — This element is frequently known as niobium. It forms a pentoxide, Cb_2O_5 (or Nb_2O_5,) which in the presence of water has weakly acid properties. The composition of the acid is H_3CbO_4. It combines with chlorine, forming the pentachloride $CbCl_5$, which decomposes with water yielding an oxychloride: —

$$CbCl_5 + H_2O = 2\,HCl + CbOCl_3.$$

Columbium also forms a trichloride, and is thus analogous to members of the nitrogen group. Columbium readily forms a double fluoride with potassium fluoride, having the composition K_2CbF_7. It also forms an oxyfluoride with potassium fluoride, having the composition K_2CbOF_5.

Praseodymium and Neodymium (At. Wts. = 140.5 and 143.6). — These elements, which for a long time were regarded as one and called didymium, occur in *samarskite, cerite, monazite; sand,* etc. Until a few years ago they were classed among the very rare substances. In the last few years they have been discovered in considerable quantity in monazite sand, in connection with the preparation of the mantles of Welsbach lights. Monazite sand has been worked

over in large quantity by Waldron Shapleigh to obtain pure cerium, lanthanum, thorium, etc., and during this work much praseodymium and neodymium have been separated in the form of the double nitrate with ammonium. More than a thousand tons of material, rich in these elements, are now in the possession of the Welsbach Light Company at Gloucester, New Jersey.

The two elements were separated from didymium by Auer Von Welsbach in 1885, by fractionally crystallizing the double nitrate with ammonium more than a thousand times.

Praseodymium forms the oxide Pr_4O_7. When this is reduced in a current of hydrogen it passes over into Pr_2O_3. Praseodymium conducts itself in many respects like aluminium, forming the sulphate $Pr_2(SO_4)_3$, and in general acting as a trivalent ion in forming salts with strong acids. Its salts are beautifully green in color, whence the name of the element.

When Von Welsbach separated didymium into its two constituents, he called the one praseodymium, from the color of its salts, and the other neodymium, or the new dymium. Neodymium forms the oxide Nd_2O_3, and the sulphate $Nd_2(SO_4)_3$. Like praseodymium, it resembles aluminium and the members of the aluminium group in forming salts in which it plays the rôle of a trivalent ion. Its salts, as already stated, are purplish-red in color, and beautifully crystallized.

Both of these elements form beautifully crystallized double nitrates with ammonium, having the composition $2(NH_4)NO_3$, $Pr(NO_3)_3\,4\,H_2O$, and $2(NH_4)NO_3$, $Nd(NO_3)_3\,4\,H_2O$.

With oxalic acid they form oxalates insoluble in dilute nitric acid, and can thus be separated from all of the more common elements.

Tantalum (At. Wt. = 183). — Tantalum, so called from the difficulties experienced in isolating it, occurs in nature with columbium, which it closely resembles in its properties. With oxygen it forms Ta_2O_5, which in the presence of water is a weak acid. The acid has the composition H_3TaO_4. Tantalum combines with chlorine, forming the pentachloride $TaCl_5$.

CHAPTER XXII

CARBON (At. Wt. = 12.0)

We now come to one of the most important elements in the whole field of chemistry. This is the first member of group IV — carbon. This element is important not only as being a great storehouse of intrinsic energy, which can readily be converted into heat, mechanical energy, light, electrical energy, etc., but as being an essential constituent of every living thing, from the simplest organism to the most complex. The number of elements which enter into living matter is not large, hydrogen, oxygen, nitrogen; sulphur and phosphorus in many cases; but carbon is always present, and is probably more closely connected with the vital functions than any other element.

Allotropic Forms of Carbon: Diamond and Graphite. — We know carbon in several modifications, both crystallized and amorphous. There are two crystalline modifications known respectively as diamond and graphite. The *diamond* is carbon and nothing but carbon, as is shown by the fact that when the diamond is burned in oxygen, it is converted completely into a compound of carbon; and when this compound is collected and weighed, the amount of carbon present in the compound is exactly equal to the weight of the original diamond.

The diamond occurs chiefly in Brazil, India, and South Africa, usually in a mica schist called *itacolumite.* To be of value as a gem it must be cut, as it is said, *i.e.* artificial faces must be ground upon it, so as to obtain the highest brilliancy. The cutting of diamonds is quite an art, especially as carried on in Amsterdam. The diamond is the hardest of all known substances, with the possible exception of boron. In order to cut it some of its own dust must be used, and for this purpose the smaller and poorer diamonds are powdered. Diamonds as they occur in nature are usually white, but black ones are frequently found.

Diamonds have now been made artificially — a problem which has attracted great attention in time past. The French chemist Moissan was the first to solve this problem as far as small diamonds

are concerned. In 1893 he prepared diamonds in connection with his beautiful investigations at very high temperatures, obtained by means of the *electric furnace.* His electric furnace is extremely simple, consisting essentially of two electrodes of carbon, terminating in the interior of two blocks of lime which fit tightly, forming the crucible in which substances are heated. Temperatures as high as 2500° can readily be produced and used, and even 3000° can be secured, but at this temperature the lime quickly melts.

In such a furnace Moissan saturated molten iron with carbon. The molten iron was poured at once into a mould which was cooled by water, and the iron quickly solidified externally. Iron saturated with carbon expands on cooling, so that as the molten interior solidifies an enormous pressure is produced. Under these conditions the carbon crystallizes in the form of small diamonds, within the iron. When the iron is dissolved in an acid, the residual carbonaceous matter contains the small diamonds. The largest diamond which Moissan has thus far prepared has a diameter of only 0.5 mm. These, however, resemble the natural diamond very closely in their hardness, their resistance to acids, crystalline form, and even the striations which occur upon them.

The preparation of large diamonds artificially is as yet an unsolved problem.

Another crystalline modification of carbon is known as *graphite or plumbago.* While the diamond is comparatively rare, graphite occurs in nature in considerable quantities, especially in Siberia. Graphite can readily be prepared by heating amorphous carbon such as ordinary charcoal in an electric furnace, or better by dissolving carbon in molten metals and allowing it to crystallize.

In order that graphite should combine with oxygen it must be heated to a very high temperature. Graphite, unlike amorphous carbon, is a very good conductor of the electric current, and like all other forms of carbon is very resistant to the action of reagents in general. Graphite is extensively used in making lead pencils.

All graphites do not seem to be the same. Indeed, there seems to be a large number of graphites which differ slightly from one another in properties.

Amorphous Forms of Carbon. — Carbon occurs in the uncrystallized condition in many forms. One of the best known is *charcoal*, or *wood charcoal* as it is usually termed. If a piece of wood is heated to a high temperature in the presence of an abundance of oxygen, the carbon unites with the oxygen, forming the well-known compound, carbon dioxide. If, on the other hand, wood is heated

without free access of air, many products are formed, but the carbon remains behind for the most part as charcoal.

Charcoal is prepared in large quantities by what is known as the destructive distillation of wood, which consists in heating wood to an elevated temperature without free access of air. In the charcoal pits the wood is placed on end in the form of a large circular pile, with small spaces between the separate pieces. The whole is then covered with earth to prevent free access of air. When the wood is burned under these conditions, the carbon does not unite with oxygen, but remains behind in the form of charcoal.

Another form of amorphous carbon is known as *coke*. This is obtained by the destructive distillation of ordinary coal without free access of air. These conditions are realized when coal is heated for the purpose of manufacturing illuminating gas, and in addition there are large plants in various parts of the world for preparing coke. In these coking-ovens coal is subjected to destructive distillation without free access of air, and coke is formed.

Bone-black is another form of amorphous carbon obtained by the destructive distillation of bones. To obtain it in pure form the inorganic matter contained in the bones is dissolved out by some strong acid. On account of its great power to absorb certain coloring matters, bone-black is extensively used to remove these substances from certain solutions, and especially from solutions of cane-sugar. In the purification of sugar enormous quantities of bone-black are used annually, the solution of sugar being slowly filtered through the bone-black. After the bone-black has become saturated with the coloring matter of the sugar it is heated again and the coloring matter destroyed. The bone-black can then be used again for purifying more sugar, and this process can be frequently repeated.

Bone-black and also wood-charcoal have remarkable powers of absorbing certain gases, especially carbon dioxide and ammonia. These substances are, therefore, frequently used to remove objectionable gases from water and other sources.

Soot or lamp-black is an amorphous form of carbon obtained by introducing a cold object into the flame of an ordinary lamp. Under these conditions some of the carbon, before it combines with oxygen, is deposited in a very finely divided condition known as lamp-black or soot. Lamp-black has a number of applications. On account of its very fine division and intensely black color it is frequently used as a coloring matter. It is also used in preparing carbon inks, which are very resistant to all chemical reagents.

Coal or stone-coal is the form in which free carbon occurs most abundantly in nature. There are great beds of these deposits in many places on the earth, and these are of fundamental importance for the welfare of the human race. In coal we find vast quantities of intrinsic energy which can readily be converted into other forms, and our steam-engines, electric motors, electric light plants, etc., are all dependent upon coal for their utility.

These deposits of coal are chiefly of vegetable origin. In certain localities where there has been a great accumulation of vegetable matter, this has undergone decomposition without free access of air, and the carbon has been deposited in the form of coal. Some of these deposits are much older than others and have been subjected, due to geological changes, to greater pressure and higher temperature. We, therefore, have different varieties of coal. If the coal is hard and comparatively free from volatile oils, it is called *anthracite;* if it is soft and contains much volatile matter, it is known as *bituminous* coal. If the process of coal formation is not very far advanced, we have *peat, lignite,* etc.

The Different Forms of Carbon contain Different Amounts of Energy. — It is obvious from the above that many forms of carbon are known. The question arises, How do these forms differ from one another? They are all carbon, and materially considered nothing but carbon, and yet have very different properties. We have met with analogous cases in the different modifications of oxygen, sulphur, and phosphorus, and found in every one of these cases that the different modifications of the same element contained different amounts of intrinsic energy. We would naturally look for the same differences in the case of carbon.

Light has been thrown on this question in the case of carbon by the experimental work of Favre and Silbermann. They measured the heats of combustion of the different modifications of carbon and obtained the following results: —

	Heat of Combustion
Charcoal	96.980 calories
Retort carbon	96.530 calories
Diamond	94.550 calories 93.240 calories
Graphite	93.360 calories

Since the end product is the same in every case — carbon dioxide — the differences between the heats of combustion of the various forms of carbon are a measure of the different amounts of intrinsic energy in these different forms.

We see that these differences are quite considerable, amorphous carbon having the largest amount of intrinsic energy and the crystallized varieties the least. The same general results which were obtained with the allotropic modifications of the other elements, also appear in the case of carbon.

Physical Properties of Carbon. — Carbon, except in the form of the diamond, is a black solid, hard, and having a more or less metallic lustre in graphite and anthracite, soft in wood charcoal and coke, and a fine powder in soot or lamp-black.

Carbon remains solid until an enormously high temperature is reached. In the electric arc, where the temperature is probably in the neighborhood of 3500°, carbon vaporizes, but even at this enormously high temperature, comparatively slowly.

The *specific heat* of carbon is anomalous, depending upon the temperature. According to the law of Dulong and Petit, the specific heat of an element multiplied by its atomic weight is a constant, 6.2. If the specific heat of carbon is taken at ordinary temperatures, this relation does not hold. It has been found, however, that the specific heat of carbon increases with rise in temperature, becoming practically constant at about 600°. This will be seen from the following results: —

Temperature	Specific Heat of Carbon
− 10°.5	0.096
58°.3	0.153
140°.0	0.222
247°.0	0.303
606°.9	0.441
806°.0	0.449

If the constant specific heat, which is obtained about 600°, is multiplied by the atomic weight of carbon, the constant is nearly obtained. The law of Dulong and Petit, then, holds as well for carbon as for any other element, provided the specific heat of carbon is taken at a temperature where it has a maximum, constant value.

COMPOUNDS OF CARBON

Carbon combines with hydrogen, oxygen, nitrogen, and sulphur, forming such a large number of compounds that a separate branch of chemistry has grown up around the element carbon. This branch, which is one of the largest of all the branches of chemistry, is known as organic chemistry. Indeed, the study of the compounds of carbon has almost absorbed the attention of chemists for the last forty years, and much of the best chemical work has been done along these lines.

While the study of the compounds of carbon belongs to organic chemistry, we shall take up a few typical, fundamental substances to give an idea of the kind of compounds which carbon forms with other elements.

Compounds of Carbon with Hydrogen.—Carbon forms with hydrogen a very large number of compounds. Indeed, these two elements form several series of compounds, the individual members of any series differing in composition by one carbon atom and two hydrogen atoms. The simplest compound of carbon and hydrogen has the composition CH_4, and is known as marsh gas, or *methane*. There is a whole series of compounds closely related to methane, and known as the methane series. The simpler members are—

Methane	CH_4
Ethane	C_2H_6
Propane	C_3H_8
Butane	C_4H_{10}
Pentane	C_5H_{12}
Hexane	C_6H_{14}

Carbon forms with hydrogen a compound containing just twice as much carbon in proportion to the hydrogen as methane. This compound has the composition C_2H_4, and is known as *ethylene*. This, like methane, is a fundamental substance, and the first member of a group of hydrocarbons which have a constant difference in composition by a constant amount. The first few members of this group are—

Ethylene	C_2H_4
Propylene	C_3H_6
Butylene	C_4H_8

Such series of compounds as the above, in which successive members differ in composition by the group CH_2, are known as *homologous series* of compounds. The above series, of which several members are known, is the ethylene series of hydrocarbons.

Carbon forms with hydrogen another series of compounds containing still more carbon with respect to hydrogen. The first member of this series is known as *acetylene*, and has the composition C_2H_2. A few members are given: —

Acetylene	C_2H_2
Allylene	C_3H_4

Carbon forms with hydrogen still another series of compounds, containing even more carbon in proportion to hydrogen than acetylene. The first member of this series of compounds is known as *benzene*, and has the composition C_6H_6. A few of the succeeding members are —

Benzene	C_6H_6
Toluene	C_7H_8
Xylene	C_8H_{10}

The members of this series of compounds differ fundamentally in their properties from those of the three series already considered. This series is, therefore, not to be regarded as an extension of the other three series in the direction of more carbon and less hydrogen. It would lead too far to discuss the nature of this difference.

Compounds of Carbon with Oxygen. — Carbon forms three compounds with oxygen; carbon monoxide, CO, containing in the molecule one atom of carbon and one of oxygen; carbon dioxide, CO_2 and carbon suboxide, C_3O_2.

Carbon Monoxide, CO. — Carbon monoxide is formed by the direct union of the two elements. When carbon is heated in a limited supply of oxygen, the product is carbon monoxide. It is also formed by the action of highly heated carbon on carbon dioxide, —

$$CO_2 + C = 2\,CO,$$

by the action of highly heated carbon on water-vapor, —

$$H_2O + C = H_2 + CO,$$

and in many other reactions. The most convenient method, however, of preparing carbon monoxide is by heating formic acid, a compound having the composition H_2CO_2 with sulphuric acid. This decomposes as follows: —

$$H_2CO_2 = H_2O + CO_2.$$

Carbon monoxide is a colorless, poisonous gas. When breathed into the system it combines with the hæmoglobin of the blood and prevents the latter from carrying out its normal function, which is

to carry oxygen to the various organs of the body. Its presence in the blood can be detected by certain characteristic bands in the absorption spectrum.

Carbon monoxide is frequently formed in the incomplete combustion of carbon in poorly ventilated furnaces. From such furnaces it easily escapes into the room, and is breathed by the inhabitants. If the room into which carbon monoxide is escaping is poorly ventilated, bad results may follow.

Carbon monoxide combines directly with oxygen, forming carbon dioxide, and is, therefore, a good reducing agent. When carbon monoxide is brought in contact with the hot oxides of the heavy metals, they are reduced to the metallic condition, and the carbon monoxide is oxidized to carbon dioxide.

When carbon monoxide is brought in contact with chlorine, and the mixture exposed to sunlight, the two combine and form the compound $COCl_2$, which is known as *phosgene.*

Carbon monoxide has the power of combining directly with certain metals, forming remarkable compounds. With finely divided nickel heated to 100° carbon monoxide combines forming *nickel tetracarbonyl:* —

$$Ni + 4\,CO = Ni(CO)_4.$$

With iron it forms the *pentacarbonyl,* $Fe(CO)_5$.

Carbon monoxide was one of the substances which remained unliquefied for a long time. This was on account of its low critical temperature, —139°.5. The critical pressure is only 35.5 atmospheres. Carbon monoxide has a boiling-point of −190°, which is very low. At a little lower temperature, −211°, it solidifies.

Thermochemistry of Carbon Monoxide.—When carbon is burned to carbon monoxide, the amount of heat set free is only about 2000 calories, while 6000 calories are liberated when carbon monoxide is oxidized to carbon dioxide. Carbon monoxide therefore contains a large amount of intrinsic energy which can be converted into heat by simply oxidizing it to carbon dioxide. It is due to this fact that carbon monoxide is an excellent heating agent, and, further, is an important constituent of illuminating gas.

Water-gas.—It has already been mentioned that one of the methods for preparing carbon monoxide is to pass water-vapor over highly heated carbon, the reaction which takes place being—

$$C + H_2O = CO + H_2.$$

This mixture of carbon monoxide and hydrogen would have very little value as an illuminating gas, since both of these gases burn

with a comparatively colorless flame, although they evolve an enormous amount of heat. This mixture of gases is passed through highly heated petroleum-vapor, and is thus mixed with hydrocarbons and other substances which give off an abundance of light when they are burned. This mixture, known as *water-gas,* is now used largely for illuminating purposes.

In preparing this gas, coal is heated to a very high temperature in the presence of the air. Water-vapor is then forced over the highly heated carbon, when the decomposition takes place in the sense of the above equation. When the coal has become cooled to a temperature which is too low, it is again heated in contact with the air, steam again passed in, and the process thus continued until the coal has been used up.

Water-gas is now extensively used where illuminating gas, made by the dry distillation of coal, was formerly employed.

Carbon Dioxide, CO_2. — The highest product of the direct oxidation of carbon is carbon dioxide. This compound occurs in a number of places in the free condition. It is one of the constituents, as will be remembered, of atmospheric air. It also occurs dissolved, in greater or less quantity, in water. Carbon dioxide escapes from the earth, in certain localities, either in the free condition or dissolved in water. The famous "dog's grotto," of Naples, is an example. When a dog or small animal enters this grotto it quickly experiences suffocation, while a man is not seriously inconvenienced. This is due to the fact that carbon dioxide is heavier than air and settles to the bottom of the grotto. It is, therefore, felt more seriously by the smaller animals than by man.

Carbon dioxide escapes from certain mineral springs, dissolved in the water of such springs. It is often present in such large quantity as to cause the water to be under considerable pressure. When the water reaches the surface of the earth, a part of the gas escapes and gives the characteristic effervescence.

Carbon dioxide is given off by animals, as can be readily shown by breathing for a short time into lime water, or a solution of barium hydroxide, when insoluble calcium or barium carbonate is formed.

Carbon dioxide is also set free when animal and vegetable matter decomposes, and also in many processes of fermentation.

Preparation of Carbon Dioxide. — Carbon dioxide can be prepared by a number of methods. Theoretically, one of the simplest methods is to burn carbon in an excess of air: —

$$C + O_2 = CO_2.$$

Practically, a far more convenient method of preparing carbon dioxide is to treat a carbonate with an acid. Carbon dioxide in the presence of water and a strong alkali, forms two series of salts which have the general composition $MHCO_3$, and M_2CO_3. When these salts are treated with an acid, we suppose that the compound H_2CO_3 is set free. This compound, however, is unstable, and breaks down at once into water and carbon dioxide, which is liberated.

Carbonates are decomposed, yielding carbon dioxide, not only by strong acids, but even by very weak acids, such as acetic. This is due to the fact that carbon dioxide is a gas, — is volatile, — and it is a general law of chemistry, that whenever a volatile compound can be formed, it is formed.

The reaction between acids and carbonates, both acid and neutral, would be represented thus: —

$$K_2CO_3 + 2\,HCl = 2\,KCl + H_2O + CO_2,$$
$$KHCO_3 + HCl = KCl + H_2O + CO_2.$$

When certain compounds are heated they readily lose carbon dioxide, while others lose it only at high temperatures. The carbonate of calcium, or ordinary limestone, or marble, belongs to the former class. When this substance is heated it breaks down thus: —

$$CaCO_3 = CaO + CO_2.$$

Chemical Properties of Carbon Dioxide. — The most characteristic chemical property of carbon dioxide is its power to form salts in the presence of aqueous solutions of alkalies. When one equivalent of caustic potash, in water, is brought into the presence of one equivalent of carbon dioxide, the following reaction takes place: —

$$KOH + CO_2 = KHCO_3.$$

When two equivalents of caustic potash are used, we have the following reaction: —

$$2\,KOH + CO_2 = K_2CO_3 + H_2O.$$

The first salt is acid potassium carbonate, the second normal potassium carbonate.

Carbon dioxide in the presence of water acts, then, as a dibasic acid. It dissolves readily in water, the amount dissolved depending upon the pressure to which the gas is subjected. The aqueous solution reacts slightly acid, showing that there are a small number of hydrogen ions present: —

$$H_2CO_3 = \overset{+}{H},\ H\overset{-}{C}O_3.$$

The acid is so weak, and its aqueous solutions have such slight conductivity, that we are not justified in assuming that there is any dissociation of the ion, $H\bar{C}O_3$, in the presence of water alone. When an alkali is present, and all the hydrogen ions from the first stage of dissociation are used up, it is probable that the ion $H\bar{C}O_3$ begins to dissociate thus: —

$$H\bar{C}O_3 = \overset{+}{H}, \overset{=}{C}O_3,$$

and this dissociation continues to the end if there are enough hydroxyl ions from the base present to combine with all the hydrogen ions as rapidly as they are formed.

The carbonates, like the salts of all weak acids, are *hydrolyzed by water.* This is shown by the fact that a salt like sodium carbonate shows a strongly alkaline reaction, which means that there are hydroxyl ions present: —

$$Na_2CO_3 + H_2O = \overset{+}{Na}, \bar{O}H + \overset{+}{Na}, H\bar{C}O_3.$$

The hydrolysis of carbonates is by no means complete, only a comparatively small number of molecules being broken down by the water as represented in the above equation.

Carbon dioxide is a very stable compound, holding its oxygen firmly. It can, however, be made to give it up under certain conditions. Certain metals, such as zinc, at a very high temperature can remove half of the oxygen from carbon dioxide, converting it into carbon monoxide.

REDUCTION OF CARBON DIOXIDE BY PLANTS

Carbon dioxide is being continually reduced by the green plants in the sunlight. They build up the carbon into complex compounds with hydrogen, oxygen, and perhaps nitrogen, and these compounds contain enormous amounts of intrinsic energy. The carbon dioxide obtained by plants comes largely from animals which give it off when they breathe, as we have seen. Plants give off oxygen, which is just what is needed by the animal world.

The complex compounds of carbon are consumed by animals, which decompose these substances into much simpler ones, especially into carbon dioxide and urea, a compound having the composition CON_2H_4. The large excess of intrinsic energy in the complex compounds over that in the simpler products which animals excrete, is converted into heat and by the animal into mechanical work.

The chief source of the energy which animals expend is, then, the complex compounds of carbon, which are built up by plants from

the simpler substance carbon dioxide, and which are broken down in the animal body into simpler substances which contain much less intrinsic energy.

It is of interest to note that most of the carbon in animal and vegetable tissues ultimately passes off when these decay, in the form of carbon dioxide. The carbon dioxide is again taken up by the plant, converted into complex compounds, consumed by the animal, broken down into simpler substances, and the cycle is thus completed.

Physical Properties of Carbon Dioxide. — The gas carbon dioxide can be readily liquefied, since its critical temperature is as high as 31°. Its critical pressure is 73 atmospheres. At lower temperatures it is liquefied at much lower pressures. At 10° the pressure required to liquefy carbon dioxide is only about 27 atmospheres, while this is reduced to 18 atmospheres at − 30°. Carbon dioxide is liquefied on a large scale by pumping it into thick-walled, steel cylinders, which are kept cool. Such cylinders are kept in the laboratory as sources of supply of carbon dioxide.

When the carbon dioxide is allowed to escape from such cylinders through a fine opening, part of it volatilizes and escapes as gas, while the remainder is converted into the solid condition and can be caught in a bag placed over the jet. Solid carbon dioxide is a compact, white mass resembling compressed snow. It has been extensively used as a refrigerating agent. When solid carbon dioxide is mixed with ether it vaporizes rapidly and a low temperature is produced. When this mixture is allowed to evaporate on the air a temperature of − 80° results, and when vaporized under diminished pressure temperatures as low as − 100° to − 110° can be readily produced.

The liquefaction of carbon dioxide is of interest and importance in connection with the liquefaction of gases in general. It was first converted into a liquid in 1834 by Thilorier, who demonstrated the refrigerating power of the mixture of solid carbon dioxide and ether. Such a mixture bears the name of its discoverer and is known as *Thilorier's mixture.*

Discovery of Critical Temperature and Pressure. — Cagnaird de la Tour observed in 1822 that ether and alcohol pass completely into vapor in a very small space, when the temperature is above a certain point. Also, that two volumes of ether volatilize at the same temperature as one volume into the same space. This made it probable that there was a temperature above which these liquids could not remain in the liquid state, but would pass over into vapor regardless of the pressure. This observation made but little impression, until

Andrews showed much later (1869) that there is a temperature for every gas, above which it cannot be liquefied. This temperature was called by Andrews the *critical temperature* of the gas. The work of Andrews was done largely with carbon dioxide. When the tube containing this gas was brought to a temperature of 13°.1, and the gas subjected to a pressure of 48.9 atmospheres, a liquid began to appear, and the volume of the gas continued to diminish without any considerable increase in the pressure being required. At 21°.5 similar results were obtained. At somewhat higher temperatures, however (31°.1 and 32°.5), results of a very different character manifested themselves. Although there was a marked decrease in volume at a certain definite pressure, yet no liquid separated. There was no evidence that any liquid had been formed. At still higher temperatures the abruptness of change in volume at any definite pressure became less and less, and entirely disappeared at 48°.1. These results are seen conveniently by plotting them in curves; the abscissas being volumes, the ordinates pressures.

The curve for 13°.1 shows that when a pressure of nearly 50 atmospheres is reached, the volume diminishes very greatly without any marked increase in pressure. This means that the gas has passed over into liquid at this pressure. The curve for 21°.1 is similar to the above curve. An abrupt transition from gas to liquid takes place, but at a higher pressure. The curves for 31°.1, 32°.5, and 35°.5 show less and less abruptness, but at none of these temperatures is any liquid produced. The curve at 48°.1 shows no break, being perfectly smooth throughout. The temperature above which carbon dioxide cannot be liquefied, was found by Andrews to be 30°.92, and this is, therefore, the critical temperature of the gas.

The temperature above which a gas cannot be liquefied has been termed by Mendeléeff the *absolute boiling-point of the gas.* This is obviously the same as Andrews's critical temperature.

The pressure which will just liquefy the gas at the critical temperature has been termed the *critical pressure.* The substance has a certain definite density under these conditions, and this is its *critical density.* The reciprocal of the critical density is the *critical volume.*

The critical temperatures and pressures of some well-known liquids are given in the following table:—

	Critical Temperature	Critical Pressure
Hydrogen	—225°.0	15.0 atmospheres
Nitrogen	—146°.0	35.0 atmospheres
Carbon monoxide . . .	—141°.0	36.0 atmospheres
Argon	—120°.0	40.0 atmospheres
Fluorine	—121°.0	50.6 atmospheres
Oxygen	—118°.8	50.8 atmospheres
Methane	— 95°.5	50.0 atmospheres
Carbon dioxide . . .	31°.0	75.0 atmospheres
Ammonia	130°.0	115.0 atmospheres
Chlorine	144°.0	83.9 atmospheres
Bromine	302°.2	

The examples given in this table show the great differences in the critical temperatures of different liquids. It also shows that the critical pressures of liquids are, in general, not high. If the temperature of the gas is below the critical temperature, the pressure required to liquefy the gas is below the critical pressure. In the liquefaction of gases, then, low temperature is far more important than high pressure. Indeed, the temperature must be at least down to the critical temperature. If the temperature is still lower, very slight pressure may liquefy the gas. We can now see why the earlier experimenters were not successful when they tried to liquefy such gases as oxygen, nitrogen, hydrogen, etc. They used in some cases enormous pressures, amounting to thousands of atmospheres, but did not cool the gases down to the critical temperatures. After these gases were sufficiently cooled they were liquefied at moderate pressures.

Continuity of Passage from the Liquid to the Gaseous State. — It will be seen from what has been said in reference to critical temperature and pressure, that a liquid can be transformed into vapor without becoming heterogeneous at any time. If the liquid is warmed above its critical temperature, a pressure is produced which is greater than the critical pressure. The volume may now be increased to any extent, yet the substance which was originally liquid remains homogeneous. The passage from the liquid to the gas is thus perfectly continuous, and it is impossible to say where the liquid state ends and the gaseous begins. The condition of matter at and near the critical point has always perplexed men of science, and many opinions have been expressed concerning it. Andrews discussed this condition in connection with carbonic acid. He pointed

out that if this gas above the critical temperature is subjected to a pressure considerably above the critical pressure, there is an enormous decrease in volume. The carbon dioxide under this condition is neither gas nor liquid, but occupies a position between the two.

Just as a liquid can be transformed into a gas without any break in continuity, so can a gas be transformed into a liquid by a continuous process. The gaseous and liquid states, then, approach as the critical point is reached, and either can be made to pass into the other without any breach in continuity.

The Kinetic Theory of Liquids.—The close relation which we have just seen to exist between liquids and gases has led to the application of the kinetic theory of gases also to liquids. Since the passage from a liquid to a gas, and *vice versa*, under certain conditions is so gradual that we cannot say where the one state of aggregation ends and the other begins, it is highly probable that any theory which obtains for the one state would apply, to some extent at least, to the other.

The liquid state, as we have seen, represents matter in a much more concentrated condition than the gaseous state. There is a much larger number of molecules in a given volume of a liquid, and, consequently, the collisions between the moving molecules are much more frequent. There would thus result in the liquid an enormous pressure, were it not for the attractive forces between the molecules. These attractive forces hold the molecules together and prevent them from flying off with explosive violence. Only those molecules which approach the surface of the liquid with unusually great velocity, can so far escape from the attractions of the other liquid molecules as to fly off into the space above the liquid. This explains the existence of vapor above every liquid. We know, however, that if these molecules fly off into a closed space above the liquid, the vapor-pressure thus produced cannot exceed a certain limit at any given temperature. We can clearly see the reason for this in terms of our theory. The molecules of the vapor, in their movements through the confining space, come in contact with the surface of the liquid. Some of these are continually coming within the range of the attractive forces of the liquid molecules, and are drawn down, as it were, into the liquid again. There is thus a continual exchange going on between the liquid and the vapor, some liquid particles passing off as vapor, and some vapor particles condensing as liquid, until a condition of equilibrium is reached. Equilibrium is established when the vapor-pressure has reached such a point that the same number of gaseous molecules are condensed in any unit of time as there are liquid mole-

cules converted into vapor. We have seen that it is only the molecules with the greatest kinetic energy which can so far overcome the molecular attractions as to escape from the liquid as vapor, and this of course lowers the mean kinetic energy of the liquid. We know that when a liquid evaporates, the mean kinetic energy of the liquid molecules decreases, or, as we say, the temperature is lowered. If the liquid is in such a position that it can absorb heat, it does so; and the heat required to effect complete vaporization of a liquid is very great. This explains why the vapor-tension of a liquid is increased with rise in temperature. The addition of heat increases the kinetic energy of the liquid molecules, and more are capable of overcoming the molecular attractions and flying off as vapor in a given unit of time. The number of molecules in the condition of vapor is therefore greater, and the vapor-pressure is greater the higher the temperature.

Carbon Suboxide, C_3O_2. — This compound has very recently been prepared by the action of phosphorus pentoxide on ethylmalonate, $CH_2(COOC_2H_5)_2 = 2\,C_2H_4 + 2\,H_2O + C_3O_2$, the phosphorus pentoxide taking up the water. Carbon suboxide is a colorless liquid boiling at 7°. It is unstable, undergoing decomposition at ordinary temperatures.

Compounds of Carbon with Oxygen and Hydrogen. — Thousands of such compounds are known. While these belong strictly to the subject of organic chemistry, a few typical substances will be considered here.

The *alcohols* are among the simplest of the compounds of carbon with oxygen and hydrogen. The first member of this series of compounds is methyl alcohol, CH_4O, or wood spirit, as it is termed. The alcohols form a homologous series of compounds which are analogous to the hydrocarbons. The first members of this series are —

Methyl alcohol . . .	CH_4O	Propyl alcohol . . .	C_3H_8O
Ethyl alcohol . . .	C_2H_6O	Butyl alcohol. . . .	$C_4H_{10}O$

If we regard methyl alcohol as the first product of the oxidation of methane, ethyl alcohol is a similar oxidation product of ethane, propyl alcohol of propane, and so on, the two series running strictly parallel.

The first step in the oxidation of ethane, C_2H_6, is ethyl alcohol, C_2H_6O; the second step in the oxidation is *aldehyde*, C_2H_4O. This is ethyl aldehyde, the second member of a homologous series of aldehydes. The first members of this series are —

Formic aldehyde .	$HCOH$	Propyl aldehyde .	C_2H_5COH
Ethyl aldehyde . .	CH_3COH	Butyl aldehyde . .	C_3H_7COH

Another product of the oxidation of a hydrocarbon is an *ether.* Take ordinary ethyl ether. This has the composition $C_4H_{10}O$, and is a member of a homologous series of compounds. The first member is methyl ether, C_2H_6O, the second methyl-ethyl ether, and so on.

If an aldehyde is further oxidized it passes over into an *acid,* and we have homologous series of organic acids, only one of which will be considered here. If ethyl aldehyde is further oxidized we have acetic acid, CH_3COOH. This is the second member of the formic acid series, formic acid being the first: —

Formic acid	$HCOOH$
Acetic acid	CH_3COOH
Propionic acid	C_2H_5COOH
Butyric acid	C_3H_7COOH

Another homologous series of compounds which carbon forms with oxygen and hydrogen is known as the *ketones.* Of these, ordinary acetone, $CH_3-CO-CH_3$, is an excellent example. Still another series is the *ethereal salts* or *esters,* of which ethyl acetate, $CH_3COOC_2H_5$, is a type; and there are many more such series of compounds, but it would lead too far to even mention them in this connection.

Compounds of Carbon with the Halogens. — Carbon combines directly with fluorine, forming carbon tetrafluoride, CF_4. It does not combine directly with any of the other halogens, but forms compounds with them by indirect methods. Thus, carbon combines with chlorine, forming *carbon tetrachloride,* having the composition CCl_4. This is formed by the action of chlorine on methane in the sunlight. The hydrogen of the methane is replaced atom by atom by chlorine.

$$(1)\quad CH_4 + Cl_2 = HCl + CH_3Cl,$$
$$(2)\quad CH_3Cl + Cl_2 = HCl + CH_2Cl_2,$$
$$(3)\quad CH_2Cl_2 + Cl_2 = HCl + CHCl_3,$$
$$(4)\quad CHCl_3 + Cl_2 = HCl + CCl_4.$$

The final product is carbon tetrachloride, the intermediate products being monochlormethane, dichlormethane, and trichlormethane or chloroform.

When carbon tetrachloride is treated with one equivalent of water, *phosgene gas* is formed: —

$$H_2O + CCl_4 = 2\,HCl + COCl_2.$$

Carbon tetrachloride is a liquid boiling at 77°, and solidifying at − 25°.

Just as we may have chlorine substitution products of the hydrocarbons, so we may have bromine, iodine, and fluorine substitution products, and all are known. The limit in these cases is reached in the compounds CBr_4, CI_4, and CF_4.

Compound of Carbon with Sulphur, CS_2. — Carbon disulphide, CS_2, is formed by passing the vapors of sulphur over highly heated carbon. The two elements unite, forming carbon disulphide, which being very volatile passes out of the field of action. Carbon disulphide is easily inflammable, readily uniting with oxygen and forming carbon dioxide and sulphur dioxide. Carbon disulphide is an excellent solvent, not only for oils, fats, and other complex organic compounds, but for bromine and iodine and many other substances. It is a liquid with a highly disagreeable odor, boiling at 46° and solidifying at − 113°. It refracts light very strongly, having an index of refraction varying with the wave-length of the light from 1.6 to 1.7.

One further feature in connection with its formation directly from carbon and sulphur should be pointed out. The reaction in which it is produced is strongly endothermic, there being considerable heat absorbed when the two elements unite.

When carbon disulphide is treated with an alkaline sulphide the two unite: —

$$M_2S + CS_2 = N_2CS_3,$$

forming a salt of *trithiocarbonic acid.* The acid of which this substance is a compound has the composition H_2CS_3, and is obviously carbonic acid in which the oxygen is replaced by sulphur. It is known as *trithiocarbonic acid* and its salts as *trithiocarbonates.* The potassium salt of this acid is used for destroying the louse which is so injurious to the grape-vine.

Compound of Carbon with Nitrogen — Cyanogen, $(CN)_2$. — When we consider the inert nature of the element nitrogen, it is surprising that the compound CN should be capable of existence. The two elements, however, do not combine directly, but combine readily with an alkali metal, forming such compounds as potassium cyanide, KCN. Cyanogen is not so readily obtained from the potassium compound, but is very easily prepared from mercuric cyanide. This compound when heated breaks down into mercury and cyanogen: —

$$Hg(CN)_2 = Hg + (CN)_2.$$

Cyanogen is a gas which is characterized by its extremely poisonous nature. Cyanogen combines directly with potassium at an elevated temperature, forming potassium cyanide. Cyanogen is quite soluble

in water. Liquid cyanogen boils at $-20°.7$, has a critical temperature of 124°, and a critical pressure of 62 atmospheres. When cyanogen is formed the action is endothermic.

Hydrocyanic Acid, HCN. — Hydrocyanic acid is formed when a cyanide is treated with an acid: —

$$MCN + HCl = MCl + HCN.$$

This acid, which is very soluble in water, is known as *prussic acid.* It is characterized by its extremely poisonous nature. Hydrocyanic acid is a very weak acid, as is shown by the small conductivity of its aqueous solutions. A few of these are given below: —

v	μ_v
4	0.33
8	0.38
16	0.43
32	0.46

It dissociates into $\overset{+}{H}$, $\overset{-}{CN}$, but only to a slight extent. When there is a strong alkali present, which is the same as to say an excess of hydroxyl ions, the hydrogen ions are used up as fast as they are formed, combining with the hydroxyl ions to form water, and more of the acid dissociates. This progressive dissociation and combination of the hydrogen ions when formed may continue until all of the acid is dissociated; and the corresponding cyanogen anions remain in the solution with the cations of the alkali in question. When such a solution is evaporated, *i.e.* when the water which causes the cyanide to dissociate is removed, the alkali cations unite with the cyanogen anions, and a cyanide is formed. Hydrocyanic acid is a liquid boiling at 27°, and melting at $-15°$.

The cyanogen group shows a very marked tendency to polymerize and form complex groups. There is a tendency to polymerize in groups of three, and especially in groups of six.

Cyanic (HOCN) and Sulphocyanic (HSCN) Acids. — Hydrocyanic acid can combine with oxygen and form cyanic acid, which has the composition HOCN. This compound shows the tendency of cyanogen to polymerize, since we have also the acids $(HOCN)_2$ and $(HOCN)_3$.

The compound formed by the addition of sulphur to hydrocyanic acid is remarkable in that it is one of the very strongest acids

known. This is shown by the conductivity of sulphocyanic acid in water: —

v	μ_v
4	337
8	345
16	352
32	358

By comparing the conductivities of sulphocyanic acid with those of hydrocyanic acid, it will be seen that by introducing a sulphur atom into the latter, we have passed from one of the very weakest to one of the strongest acids known. It is generally true, that by increasing the amount of sulphur in the molecule we increase the acidity of the compound, but not to the same extent as in hydrocyanic and sulphocyanic acids.

THE RÔLE OF CARBON IN PRODUCING LIGHT

Illumination. — The subject of the production of light or illumination is one which has attracted attention for a very long time, and is still doing so. In practically all of the earlier methods of producing light, and in many of those used to-day, carbon is employed in one form or another. Most of the methods of illumination owe their existence to some compound of carbon which is burned or oxidized, giving out heat and light. This is analogous to what we saw was taking place in the bodies of animals. The complex compounds of carbon were decomposed into much simpler substances, which contain far less intrinsic energy than the original substances. The intrinsic energy which disappeared was converted into heat, and was the chief source of heat in the animal body.

If this decomposition of complex carbon compounds, or, as we say, oxidation processes, proceed with sufficient rapidity, there is a rapid production of heat energy, and light energy results. This is what takes place in our luminous flames, whether produced by the candle, oil-lamp, gas-jet, or acetylene light.

Candle and Oil-lamp. — In the candle we have complex compounds of carbon which at ordinary temperatures are solid. These are made by melting the stearine, tallow, or paraffine, and pouring the liquid into a mould after a wick has been placed in the centre of the mould. The object of the wick is to carry by capillarity the

material of the candle, as it is melted, up into the flame by capillarity. The tip of the candle is melted, and the end of the wick ignited. This melts a portion of the solid hydrocarbons, which are carried up by the wick into the flame, are vaporized and burned, the heat set free melting more of the solid, and the process is thus a continuous one. The heat and light are derived from the breaking down of complex compounds of carbon into simpler substances, and the oxidation of the carbon to carbon dioxide.

In our oil-lamps the compounds of carbon which are to be burned are liquid at ordinary temperatures. These are carried up into the flame by means of the wick, as in the candle, and the same general processes are involved in the production of light and heat.

Coal-gas, Water-gas. — *Coal-gas* is produced, as we have seen, by the dry distillation of coal, one ton of coal yielding about 10,000 cubic feet of gas. Coal-gas consists largely of compounds of carbon with hydrogen — hydrocarbons — and free hydrogen. These are the chief source of the light and heat when coal-gas is burned.

Water-gas is produced by the action of highly heated carbon on steam, giving, as we have seen, carbon monoxide and hydrogen, and this mixture is then enriched by adding to it certain hydrocarbons. Here, again, the chief source of the light and heat are compounds of carbon, which are broken down in the flame, and the carbon oxidized to carbon dioxide.

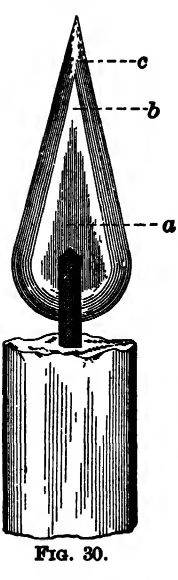


Fig. 30.

Flames and their Luminosity. — If we examine a typical flame, say that of a candle, we observe three distinct parts: an inner cone *a* (Fig. 30), of unburned gases, is surrounded by a zone *b*, of partially oxidized substances. It is in this zone that acetylene is formed, which, we shall see, has much to do with the light-giving power of the flame. This zone is the chief source of light in the flame. This is surrounded by a third layer, *c*, of burning gases, and here, where there is an abundant supply of oxygen from the air, the processes of oxidation are completed. This part of the flame is relatively only slightly luminous.

So much for the structure of a flame. The question remains, What are the causes of the luminosity of flames? We have seen that the chief source of light in a flame is in the middle zone, where the combustion is not complete. This gave rise to the theory that the chief source of light in a flame is unburned, solid particles of carbon, which become heated to incandescence. These

particles came from the compounds of carbon which are decomposed by the heat of the flame. This theory accounts for many of the facts concerning the luminosity of flames, but by no means for all.

Hydrogen gas at atmospheric pressure burns with an almost non-luminous flame. Hydrogen gas, under high pressure, however, burns with a luminous flame. The *effect of pressure on luminosity* is also shown by burning a candle in a valley and on a high mountain. Under the former conditions, where the pressure is relatively high, the luminosity is much greater. Further, gases which burn with a luminous flame can be made to burn with a relatively non-luminous flame by mixing them with an indifferent gas, or by simply cooling them.

These facts cannot by any means be all explained on the solid particle theory of luminosity. There are undoubtedly many influences which affect the luminosity of flames, so that probably no one theory can account for all of the facts connected with this phenomenon.

According to recent investigations in England, it seems very probable that the formation and oxidation of acetylene in flames is vitally connected with their light-giving power.

Bunsen Burner. — Blowpipe. — Practical use is made of the fact that complete oxidation, and also the dilution of a gas with an indifferent gas, lowers its luminosity in constructing the *Bunsen burner.* This is a piece of apparatus so frequently used in the laboratory that a few words concerning it will suffice.

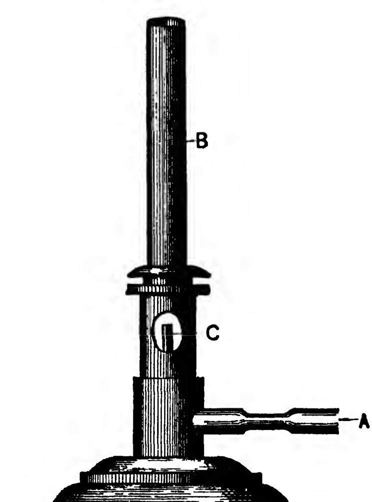


FIG. 31.

A Bunsen burner is shown in Fig. 31. The gas enters through the horizontal tube, into the vertical tube *B*. Air enters through the hole *C*, and mixes with the gas. The flame consists of two distinct parts: an inner blue cone, where the oxidation is far from complete, and which is known as the *reducing flame,* since it has remarkable power to combine with oxygen and reduce substances such as the oxides of the metals; and an outer, almost non-luminous tip, where the oxidation of the gas is completed and where the temperature is very high.

This is known as the *oxidizing flame*, on account of its power to give up oxygen to substances which can be oxidized. Metals, for example, in this flame are usually converted into oxides.

By means of the Bunsen burner very high temperatures can be secured by the combustion of illuminating gas, without the production of any appreciable quantity of light. This is due to the comparatively complete oxidation of the compounds of carbon in the gas, by the excess of oxygen in the air which is mixed with the gas. When a cold object is inserted into the flame of a Bunsen burner, no carbon is deposited upon it in the form of soot, and the lamp is, therefore, very convenient for heating where cleanliness is absolutely essential. The Bunsen burner is one of the most frequently used pieces of apparatus in the chemical laboratory.

The Blowpipe is a still more efficient means of obtaining a clean oxidizing, and a clean reducing flame, and of directing these flames where they are desired. The blowpipe itself is shown in Fig. 32. It consists of a tube, t, into which the breath is blown from the mouth, and a tube, t_1, at right angles to this, through which the air from the lungs passes into the flame. Into the top of an ordinary Bunsen burner is inserted a tube with a narrow opening, so as to give a narrow flame. The blowpipe is placed upon the upper edge of this tube as indicated in the drawing, and the breath expelled continuously through the tube. The combustion of the gases in the flame is excellent, the flame taking the form shown in the figure. The inner flame, a, is the reducing flame, and the outer tip, b, the oxidizing portion of the flame.

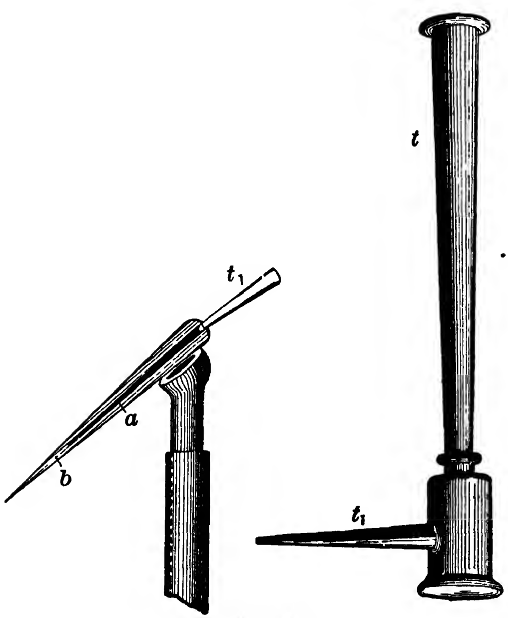


FIG. 32.

By means of the blowpipe flame very delicate work can be done. In the reducing flame small quantities of metal oxides can be reduced to the metallic condition, and identified. The blowpipe is, therefore, an aid in detecting the presence of small quantities of substances, and in skilful hands is of great assistance in qualitative analysis.

Effect of cooling the Flame. — The effect of cooling the flame can be readily shown by means of the following experiment: Open an ordinary gas stop-cock, and a short distance above the orifice hold a wire-gauze with fine mesh. Light the gas above the gauze, and it will burn without the gas below the gauze taking fire. This is due to the fact that the metallic gauze conducts the heat away so rapidly, that the gas below the gauze is not heated to its *kindling temperature*, and does not ignite.

This principle was made use of by Sir Humphry Davy in the construction of his *safety lamp*, for use in mines where explosive gases are liable to accumulate. The flame is simply surrounded by a fine wire-gauze. If the explosive gases should ignite on the inside of the gauze, the flame cannot propagate itself through the gauze, since it is too greatly cooled. The gauze, thus conducting the heat from the flame, prevents the gases on the outside from becoming heated to their kindling temperature, and thus explosions are avoided when lights are carried into an atmosphere containing explosive gases.

The Acetylene Light. — In the last few years carbon has come to play a new rôle as an illuminant. A new method has been discovered for preparing acetylene, which makes it possible to use this substance in illumination. The method of preparing acetylene is based upon the combination of carbon with many of the metals. These compounds, known as *carbides*, have recently been made in large numbers in the electric furnace by Moissan. The compound with calcium, or calcium carbide, may be taken as the type. This is formed in the electric furnace from a mixture of lime and carbon, and has the composition CaC_2. When this is treated with water, calcium hydroxide and acetylene are formed: —

$$CaC_2 + 2\,H_2O = Ca(OH)_2 + C_2H_2.$$

Since the critical temperature of acetylene is 37°, and its critical pressure 67 atmospheres, it can be readily liquefied. It is, however, not preserved in the liquid condition in cylinders, like carbon dioxide, on account of its explosive nature. It is generated as needed, by allowing water in small quantity to come in contact with calcium

carbide when acetylene is desired. By regulating the flow of water the rate of production of acetylene can be controlled. Acetylene lamps are based upon this principle.

The amount of heat which is set free when acetylene is burned is very great indeed, being for a gram-molecular weight 310,000 calories. When acetylene is completely oxidized, the products are, as we would expect, carbon dioxide and water: —

$$2\,C_2H_2 + 5\,O_2 = 2\,H_2O + 4\,CO_2.$$

The Welsbach Light. — The Welsbach light differs from the ordinary gas-light in that solid substances are introduced into the flame, which, when hot, have remarkable light-giving power. The Welsbach light depends for its value entirely upon the "mantle." The mantle consists of a mixture of thorium and cerium oxides. It is prepared as follows: Fine cotton thread is woven into exactly the form of the mantle. This is saturated with an aqueous solution of a mixture of the nitrates of thorium and cerium. This mixture contains 99 per cent of the thorium salt and one per cent of the cerium salt. The mantle is then dried and highly heated to burn out all organic matter, and to convert the cerium and thorium nitrates into the oxides. It is then ready for use.

It is a remarkable fact that if the amount of cerium salt added to the thorium is either increased or diminished appreciably, the light-giving power of the Welsbach burner is greatly diminished.

The value of the burner is to be found in the power of these oxides to convert heat energy in large quantity into light energy, so that the final result is a conversion of more of the intrinsic energy of the carbon compounds and other substances in the gas into light energy.

The Electric Light. — At first sight the relation between carbon and the electric light may not appear to be very close, other than the use of carbon as the source of energy to drive the dynamo which generates the electrical energy. Indeed, the intrinsic energy of the carbon, through the steam-engine and the dynamo, is converted into electrical energy.

To obtain light energy from electrical energy, a resistance to the passage of the electrical current is interposed. The current is usually passed between two carbon poles, which are heated to such a high temperature that the carbon is partially volatilized. At this temperature the highly heated carbon gives off an enormous amount of light energy, and this is the source of the light in the electric arc-light. In the incandescent light the carbon is heated white-hot, and gives out light without undergoing any appreciable change.

Measurement of the Relative Intensities of Light. — We are familiar with light of various degrees of intensity. Indeed, the intensity of light varies from the brightness of the sun, to light which is so feeble that it just produces a sensation when allowed to fall on our retina. It is obviously desirable that some means should be available for measuring the relative intensities of light from different sources. A number of instruments have been devised for this purpose. These are known as *photometers.*

A very simple form of photometer has been devised by Bunsen, and this will be briefly described. If a piece of paper is covered with oil in one spot, and this spot observed in transmitted light, it will allow more light to pass through than the remainder of the paper and will, therefore, appear bright. If, on the other hand, it is observed in reflected light, it will appear dark for the same reason, *i.e.* it transmits more of the light and reflects less of it. If now a light of standard intensity is placed upon one side of the spot, the light whose intensity it is desired to compare with the standard is placed upon the other side. The second light is moved towards or from the spot until the spot disappears, *i.e.* until the spot has exactly the same brightness as the remainder of the paper. When this condition is reached the spot is illuminated on the two sides with exactly equal intensity. Knowing the intensity of the standard light, its distance from the screen, and the distance of the second light from the screen, we have all the data necessary for calculating the relative intensity of the second light. Intensity of illumination is usually expressed in terms of candle-power. This means the amount of light given out by a candle of a certain composition and certain dimensions burning at a certain rate.

The science of photometry is especially useful in connection with the light-giving power of coal-gas. This is frequently tested to see whether it comes up to the desired standard.

CHAPTER XXIII

SILICON (At. Wt. = 28.4)

The second member of the fourth group in the Periodic System is silicon. This element is very widely distributed over the surface of the earth, and constitutes an important part of most rocks. Silicon occurs in great abundance as the dioxide, and forms an acid — silicic acid, whose salts make up many of our best-known rocks. Silicon dioxide, or *quartz*, also occurs in huge masses, and is a constituent of many rocks, especially *granites*, *gneisses*, etc. Silicon dioxide occurs in great abundance as *sand*, especially along the edges of large bodies of water.

The Element Silicon. — Silicon is prepared from its compounds by a number of methods. One of these consists in heating silicon tetrafluoride with sodium. $SiF_4 + 4\,Na = 4\,NaF + Si$. Another method consists in heating sodium silicofluoride Na_2SiF_6 with metallic sodium or potassium. The following reaction takes place: —

$$Na_2SiF_6 + 4\,K = 2\,NaF + 4\,KF + Si.$$

When this reaction is carried out some metallic zinc is added, which melts and dissolves the silicon when formed. The zinc is then dissolved in an acid and the crystallized silicon remains behind.

Silicon is also formed when the dioxide is heated with a metal like potassium, sodium, magnesium, etc.: —

$$SiO_2 + 4\,M = 2\,M_2O + Si.$$

Silicon unites with fluorine at ordinary temperatures forming the tetrafluoride, SiF_4. It combines with oxygen, chlorine, etc., at elevated temperatures.

Silicon exists both in the *amorphous* and *crystalline* condition. The amorphous form, obtained by the reduction of the dioxide or halide with metals, readily combines with oxygen, forming the dioxide, also reacts with hydrofluoric acid, forming silicon tetrafluoride, and combines with a strong alkali, forming a salt of silicic acid.

$$2\,KOH + Si + H_2O = 2\,H_2 + K_2SiO_3.$$

The potassium silicate formed is a salt of metasilicic acid, H_2SiO_3.

When amorphous silicon is heated to a high temperature it melts, and on solidifying is crystalline. Crystallized silicon is best obtained by dissolving molten silicon in molten zinc and allowing the mass to cool. When the zinc is dissolved in acids the silicon remains as grayish-black crystals, with a metallic lustre resembling graphite.

Crystallized silicon, which is the analogue of crystallized carbon, has very different properties from amorphous silicon. It is much less readily attacked by chemical reagents. It is not attacked by oxygen at a white heat. It is, however, attacked by fluorine at ordinary temperatures, and by chlorine at elevated temperatures, forming the fluoride or chloride of silicon. When highly heated with an alkaline carbonate it forms the corresponding silicate.

Crystals of silicon are noted for their extreme hardness.

We have in these two varieties of silicon unquestionably the analogues of amorphous and crystallized carbon.

Silicon Hydride or Hydrogen Silicide, SiH_4. — Silicon forms a compound with hydrogen, known as silicon hydride or hydrogen silicide, containing one atom of silicon united with four atoms of hydrogen. It is prepared by treating compounds of silicon with aluminium or magnesium, with an acid.

The reaction in the case of magnesium hydride is represented thus: —

$$SiMg_2 + 4\,HCl = 2\,MgCl_2 + SiH_4.$$

Hydrogen silicide thus prepared is spontaneously inflammable when it comes in contact with the air. The pure gas, however, is not inflammable at ordinary temperatures by mere contact with the air, but ignites when slightly warmed. The fact that the gas takes fire and combines with oxygen at ordinary temperatures is, therefore, probably due to small quantities of some other substance, which is present as an impurity.

As far as composition is concerned, silicon tetrahydride is analogous to methane, — SiH_4, — CH_4. The former, however, is very unstable, while the latter is quite stable. When silicon hydride is burned in the presence of the air the products are silicon dioxide and water: —

$$SiH_4 + 2\,O_2 = SiO_2 + 2\,H_2O.$$

This is also analogous to methane, which yields on combustion carbon dioxide and water.

Silicon also forms with hydrogen the compound Si_2H_6, which is spontaneously inflammable.

Silicon Dioxide, SiO_2. — Silicon forms one compound with oxygen

— silicon dioxide. This is analogous to carbon dioxide. It does not form the analogue of carbon monoxide.

Silicon dioxide occurs in nature in great abundance. It is beautifully crystalline in several varieties of quartz, such as *amethyst*, *rock crystal*, and the like, and with certain impurities which give it color it is of more or less value as gems, such as *opal*, *jasper*, *onyx*, *agate*, etc.

It occurs in great masses in less attractive forms, such as *quartz*, *sand*, *flint*, *sandstone*, and the like, and is frequently the chief constituent of large mountain ranges. When we consider the abundance of the two forms, quartz and sandstone, we can see the importance of the element silicon in the inorganic world, and from a geological standpoint. Silicon dioxide is also taken up by certain plants, but its importance in the organic world is very small as compared with the element carbon.

Silicon dioxide is very resistant to chemical reagents, and is not attacked by acids, with the exception of hydrofluoric. When powdered very finely and fused with a caustic alkali, or an alkaline carbonate, it is transformed into a silicate: —

$$SiO_2 + 2\,KOH = K_2SiO_3 + H_2O.$$

This is a salt of metasilicic acid, having the composition H_2SiO_3.

The Acids of Silicon. — Silicon combines with hydrogen and oxygen, forming a number of acids which, however, can all be regarded as derived from one mother-substance. When an alkaline silicate like that mentioned above is treated with an acid, the following reaction probably takes place: —

$$K_2SiO_3 + 2\,HCl + H_2O = 2\,KCl + H_4SiO_4.$$

This same compound is formed when silicon tetrafluoride is treated with water: —

$$SiF_4 + 4\,H_2O = 4\,HF + H_4SiO_4.$$

The compound H_4SiO_4, known as *normal silicic acid*, or *orthosilicic acid*, is a white, gelatinous mass, insoluble in water. To separate the silicic acid from impurities, such as potassium chloride, the ordinary methods of washing are not sufficient. The silicic acid forms such a finely divided, jelly-like mass that it is scarcely possible to dissolve out substances which are readily soluble in water, because of the difficulty of securing good contact between the water and the substances, and the further difficulty of removing the solution when they are once dissolved.

A new method of purification can be made use of in the case of silicic acid. This is based upon the fact that substances like the salts which easily form crystals, and many other substances, pass readily through certain vegetable membranes, while other classes of substances which do not crystallize, like silicic acid, do not pass through such membranes. If a mixture of a salt like potassium chloride and silicic acid is placed in a vessel whose bottom is closed with vegetable parchment, and the vessel dipped into water, when water is added to the mixture the salt will pass out through the parchment and the silicic acid will remain behind. An apparatus of this kind is known as a *dialyzer*, and the process as *dialysis*. Substances which pass through such a membrane, since they generally form crystals, are known as *crystalloids;* while substances which do not pass through such membranes are known as *colloids.* A large number of substances belong to the colloids. These include starch, albumen, and the finely divided metals, which will be considered later.

Silicic acid, containing crystalloids as impurities, is allowed to remain in the dialyzer for a time, and then the water in the outer and inner vessel is removed and pure water added to both vessels. This process is repeated a few times when all the crystalloids will have passed through the parchment into the outer vessel, and have thus been separated from the silicic acid.

Solutions of the colloids are not true solutions, but only *pseudo-solutions.* This is shown by the fact that they do not lower the freezing-point of the solvent, do not produce a rise in the boiling-point of the solvent, and do not exert any osmotic pressure. Since they do not exert osmotic pressure, they have no power to diffuse — diffusion being caused by osmotic pressure. This is doubtless the chief reason why the colloids do not pass through the parchment in dialysis.

When normal silicic acid is heated it loses water and passes over into *metasilicic acid:* —

$$H_4SiO_4 = H_2O + H_2SiO_3.$$

When it is further heated it loses more water and forms silicon dioxide: —

$$H_2SiO_3 = H_2O + SiO_2.$$

Silicon has the power of combining with hydrogen and oxygen, forming complex molecules which have acid properties. These are known as *polysilicic acids.* They can all be regarded as derived from the acid H_4SiO_4, by removal of one or more molecules of water from two or more molecules of the acid. Thus, by the removal of

one molecule of water from two molecules of normal silicic acid we have: —

$$2\,H_4SiO_4 = H_2O + H_6Si_2O_7.$$

By removing two molecules of water: —

$$2\,H_4SiO_4 = 2\,H_2O + H_4Si_2O_6.$$

By removing three molecules of water: —

$$2\,H_4SiO_4 = 3\,H_2O + H_2Si_2O_5.$$

From three molecules of silicic acid we may, similarly, remove one, two, three, molecules of water: —

$$\begin{aligned} 3\,H_4SiO_4 &= H_2O + H_{10}Si_3O_{11}, \\ 3\,H_4SiO_4 &= 2\,H_2O + H_8Si_3O_{10}, \\ 3\,H_4SiO_4 &= 3\,H_2O + H_6Si_3O_9, \\ 3\,H_4SiO_4 &= 4\,H_2O + H_4Si_3O_8, \\ 3\,H_4SiO_4 &= 5\,H_2O + H_2Si_3O_7. \end{aligned}$$

This series of acids, some of whose salts are known, suggest the homologous compounds of carbon. The constant difference with carbon is the group CH_2. The constant difference with silicon is the molecule of water H_2O.

Some of the salts of the polysilicic acids are very important substances, since they constitute many of the most abundant silicates.

The silicates are in general very stable, and with the exception of the alkaline silicates, very insoluble substances, and hence are not dissolved in appreciable quantities by the waters which come in contact with them.

Conversion of Silicates into Carbonates.—Notwithstanding the great stability and insolubility of the silicates, they are being decomposed all over the surface of the earth by such a weak acid as carbonic acid. This *carbonation* is taking place all over the surface of the earth, wherever the carbon dioxide in the air and in the waters comes in contact with silicates. This at first sight is very surprising. How is it possible for such a weak acid as carbonic acid to displace silicic acid from the very stable silicates? This is especially difficult to understand when we consider that carbonic acid is so easily volatile and, therefore, escapes from the field of chemical action.

The explanation is to be found in *the effect of mass on chemical activity*, as was pointed out by the German, Heinrich Rose. This is one of the very best examples of mass action, as conditioning the direction as well as the magnitude of chemical action.

The great amount of carbon dioxide in the air and in the water,

acting slowly but continually for a long period of time, effects a reaction which, in the laboratory, would be impossible.

The above process, known as the weathering of the rocks, is of great geological and economical importance. By this means in part, many of the most resistant rocks are decomposed and the surface of the earth greatly changed in appearance. This process is of tremendous economical importance in that the constituents of rocks are made available for plants. The alkalies and other substances are set free in the main as carbonates, and are either taken up by the various plants, or are *absorbed* by the soil and retained until needed by vegetation.

By absorption is meant the adhesion of solid matter to the surface of the soil particles, and this has been shown to be a valuable principle in connection with the fertilization of, and retention of, soluble materials in the soil.

We have had a number of examples of the effect of mass on chemical activity. The law which governs this action has already been formulated.

Compounds of Silicon with the Halogens.—It has already been mentioned that silicon combines with chlorine directly at an elevated temperature. The compound formed is *silicon tetrachloride*, $SiCl_4$, the analogue of carbon tetrachloride, CCl_4. The analogy extends farther, in that silicon can combine with hydrochloric acid, forming the compound $SiCl_3H$, which is known as *silicon chloroform*. This is the silicon analogue of chloroform, which is trichlormethane —CCl_3H.

Silicon combines with bromine forming the *tetrabromide*, $SiBr_4$, and also *silicon bromoform*, $SiBr_3H$, the analogue of bromoform — CBr_3H.

With iodine silicon forms the *tetraiodide*, SiI_4, and also *silicon iodoform*, SiI_3H, the analogue of iodoform CI_3H.

The compound of silicon and fluorine, SiF_4, is of special interest, since it is the compound formed when hydrofluoric acid acts on glass. *Silicon tetrafluoride* also decomposes with water, yielding an acid of remarkable composition. Silicon tetrafluoride is formed by the action of hydrofluoric acid on silicon dioxide. Since hydrofluoric acid is prepared most conveniently by the action of sulphuric acid on calcium fluoride, silicon tetrafluoride is prepared by mixing sand, calcium fluoride, and sulphuric acid.

When silicon tetrafluoride is treated with water the following reaction takes place: —

$$3\,SiF_4 + 4\,H_2O = H_4SiO_4 + 2\,H_2SiF_6.$$

The compound H_2SiF_6 is known as *hydrofluosilicic acid.* It is readily soluble in water, having strongly acid properties. With alkalies it forms salts of the composition M_2SiF_6. It is, therefore, a dibasic acid, dissociating into —

$$\overset{+}{H}, \overset{+}{H}, \overset{=}{SiF_6}.$$

When salts of hydrofluosilicic acid are heated they decompose into the corresponding fluoride and silicon tetrafluoride: —

$$M_2SiF_6 = 2\,MF + SiF_4.$$

When hydrofluosilicic acid is treated with an excess of an alkali, it decomposes in the sense of the following equation: —

$$H_2SiF_6 + 6\,MOH = 6\,MF + 2\,H_2O + Si(OH)_4.$$

The salts of hydrofluosilicic acid are generally soluble in water, with the exception of certain salts of the alkalies and alkaline earth metals. These will be considered later.

Compound of Silicon with Carbon — Carborundum. — From the many analogies between silicon and carbon, we would not expect these two elements to combine and form any very stable compound. The facts are, however, quite different. Silicon and carbon form a very stable compound, as is shown by the method of its preparation. When finely powdered sand is mixed with carbon and sodium chloride, and the mixture subjected to the highest temperature of the electric furnace (3500°), the following reaction takes place: —

$$3\,C + SiO_2 = 2\,CO + SiC.$$

Carborundum is characterized by its extreme hardness, and is useful technically on account of this property. It is extensively used to cut glass, and in other connections where the diamond was formerly employed. It is very resistant to chemical reagents, not being attacked to any appreciable extent by any of the acids. When fused with the strong alkalies it is decomposed. When powdered and heated in a stream of oxygen, the carbon is burned out only with great difficulty.

CHAPTER XXIV

GERMANIUM, TITANIUM, ZIRCONIUM, CERIUM, THORIUM

Next to silicon, in group IV, comes germanium, which will be briefly studied. Then come tin and lead, which will be taken up much later under the metals. The four elements, titanium, zirconium, cerium, and thorium, will be dealt with in the present connection.

Germanium (At. Wt. = 72.5). — Germanium is of interest in that it was one of the elements predicted by Mendeléeff from the Periodic System. It was discovered in 1886 by Clemens Winkler, in the mineral *argyrodite*, which is the double sulphide of silver and germanium, $4\,Ag_2S.GeS_2$.

The element germanium is formed by reducing the oxide with metallic magnesium, magnesium oxide and germanium resulting. It forms two series of compounds, in one of which it is bivalent and in the other quadrivalent. The more important of the bivalent compounds of germanium are the hydroxide, $Ge(OH)_2$, and the sulphide, GeS.

The tetravalent compounds of germanium resemble those of silicon. It forms the dioxide GeO_2, the tetrahydrate $Ge(OH)_4$, the tetrachloride $GeCl_4$, the tetrafluoride GeF_4, the disulphide GeS_2, and so on. The analogy to silicon is further shown in the compound K_2GeF_6, which is the analogue of K_2SiF_6.

Titanium (At. Wt. = 48.1). — Titanium occurs in fairly large quantities, and is widely distributed over the surface of the earth. It occurs in the minerals *titanite, rutile, bauxite*, etc. Titanium combines with oxygen, forming the compounds TiO, Ti_2O_3, and TiO_2.

It forms, with oxygen and hydrogen, titanic acid $Ti(OH)_4$, which is the analogue of silicic acid. It also loses water and forms metatitanic acid, H_2TiO_3, the analogue of metasilicic acid.

Like carbon, titanium forms the tetrachloride $TiCl_4$. It also forms the trichloride $TiCl_3$ and the dichloride $TiCl_2$.

The analogy to silicon is shown in the compound potassium titanofluoride K_2TiF_6, which is the analogue of potassium silico-

fluoride. Titanium also combines with carbon, forming titanium carbide TiC, which is the analogue of silicon carbide, carborundum.

Zirconium (At. Wt. = 90.6). — The element zirconium occurs chiefly as the silicate $ZrSiO_4$. This is the beautifully crystallized mineral *zircon*. Zirconium acts as a tetravalent element, forming the hydroxide $Zr(OH)_4$, the chloride $ZrCl_4$, the sulphate $Zr(SO_4)_2$, and so on. Zirconium forms the dioxide ZrO_2, also the analogous carbide ZrC_2. It also forms the compound H_2ZrF_6 — *Hydrofluozirconic acid*, the analogue of hydrofluosilicic acid.

Cerium (At. Wt. = 140.25). — Cerium is one of that group of rare elements which occurs in *monazite sand*. The element is obtained by electrolyzing the chloride. While cerium forms with oxygen the dioxide CeO_2, it acts in most of its compounds as a trivalent element. Thus, it forms the chloride $CeCl_3$, the sulphate $Ce_2(SO_4)_3$, the nitrate $Ce(NO_3)_3$. The double nitrate of cerium and ammonium, $2\,Ce(NO_3)_3$, $3\,NH_4NO_3 + 10\,H_2O$, is a beautifully crystallized substance.

Cerium can, however, form compounds in which it acts as a tetravalent element, the compound $Ce(SO_4)_2$ being known. As already mentioned, cerium is used in small quantity in preparing the mantles of Welsbach burners.

Thorium (At. Wt. = 232.5). — Thorium is another of the rare elements which occur in monazite sand. It also occurs as the silicate, *thorite*, and in many other minerals such as *gadolinite*, *samarskite*, etc. It forms the hydroxide $Th(OH)_4$.

As has already been mentioned, thorium is the chief constituent of the Welsbach mantle. Thorium compounds have been shown to be radioactive.

CHAPTER XXV

BORON (At. Wt. = 11.0)

We pass now to group III of the Periodic System, the first member of which is boron. This is the only member of this group which has distinctly acid-forming properties. We shall, therefore, take up boron in the present connection, and the remaining members of the group considerably later when we come to study the base-forming, or metallic, elements.

Occurrence, Preparation, and Properties. — The borates, or salts of boric acid, are the chief source of the element boron. We should mention especially *boracite, borocalcite,* and *borax.*

Boron is prepared by the reduction of the trioxide of boron. When borates are treated with a strong acid, boric acid, H_3BO_3, is liberated. This loses water on heating, forming the trioxide: —

$$2\,H_3BO_3 = 3\,H_2O + B_2O_3.$$

The oxide is reduced by potassium, magnesium, etc., at a high temperature, the oxygen combining with the metal and setting free the boron. In preparing boron the nitrogen of the air must be excluded by a layer of borax, since nitrogen combines with boron at high temperatures. Boron forms beautiful crystals, which are characterized by their great hardness. They seem to have about the same hardness as the diamond. Crystallized boron combines with oxygen only slowly, even at very high temperatures. It unites with chlorine at elevated temperatures. It is not attacked at ordinary temperatures either by acids or alkalies.

Amorphous boron is much less resistant to chemical reagents. It is much more easily oxidized, and far more readily attacked by acids and alkalies than the crystallized form.

It will be remembered that boron is one of the elements whose *specific heat* does not conform to the law of Dulong and Petit. The specific heat of boron as determined at ordinary temperature was too small to accord with the law of Dulong and Petit. It was, however, found that the specific heat of boron increases with the temperature,

until a temperature of about 500° is reached. The specific heat then becomes constant and accords very well with the law.

Boron Trioxide, B_2O_3. — The compound of boron and oxygen, boron trioxide, B_2O_3, is formed either by removing water from boric acid —

$$2\,H_3BO_3 = 3\,H_2O + B_2O_3,$$

or by burning boron in oxygen, when the two elements unite and form the trioxide: —

$$2\,B + 3\,O = B_2O_3.$$

Boron trioxide, as seen by the first method described for its preparation, is an anhydride of boric acid, which we shall now study.

Boric Acid, H_3BO_3. — Boric acid occurs in nature in the free condition. It is volatile with water-vapor, and in the region of certain hot springs, as in Tuscany, it is brought to the surface of the earth by the escaping vapors.

Boric acid is soluble in water, forming beautiful, white crystals when the aqueous solution is evaporated. It is easily recognized by the fact that its alcoholic solution burns with a characteristic green flame. If boric acid, or a borate treated with sulphuric acid, is treated with a little alcohol and the alcohol ignited, the flame appears green throughout if there is much boric acid present. If only a small amount of boric acid is present the flame is green only on the edges.

The salts of the normal boric acid, H_3BO_3, do not exist. When boric acid is heated, however, it loses water and passes over into another acid, whose salts are well known. The first product of the dehydration of boric acid is *metaboric acid* — HBO_2: —

$$H_3BO_3 = H_2O + HBO_2.$$

Boric acid can, however, lose water in a different manner and form an acid whose salts are well known: —

$$4\,H_3BO_4 = 5\,H_2O + H_2B_4O_7.$$

The acid $H_2B_4O_7$ is known as *tetraboric acid*, and its sodium salt, $Na_2B_4O_7$, is ordinary borax. Borax melts easily, forming a colorless liquid. This liquid has the power of dissolving certain metal oxides and forming with them, when cold, glass-like masses which have characteristic colors. The borax bead is, consequently, of importance in blowpipe analysis for the detection of metals.

Boron Nitride, BN. — Boron combines with nitrogen, forming the compound BN. Amorphous boron, when heated to a high tempera-

ture in the presence of nitrogen, combines with it and forms the nitride. Boron nitride is an amorphous solid, very resistant to chemical reagents. Boron nitride, when heated in the air, becomes phosphorescent; with water-vapor it decomposes into ammonia and metaboric acid. The existence of this compound makes it necessary, in preparing boron, to protect the element, when formed at the high temperature, from the air, otherwise the boron will combine in part with nitrogen, and the result will be a mixture of boron and boron nitride.

Compounds of Boron with Other Elements. — Boron combines with a number of the elements. With chlorine it forms the trichloride BCl_3, with bromine the tribromide BBr_3, with iodine the triodide BI_3, and with fluorine the trifluoride BF_3. Boron also combines with sulphur, forming the trisulphide B_2S_3.

Boron forms a salt with phosphoric acid having the composition BPO_4.

In the above compounds boron acts as a basic element.

Summary. — We have studied thus far oxygen, hydrogen, and the halogens or members of group VII, in the Periodic System. The analogues of oxygen; sulphur, selenium and tellurium, in group VI, were then taken up. The remaining members of group VI are so distinctly metallic that they will be studied with the metals. The entire group V was then studied, and all of group IV, with the exception of the important metals, tin and lead.

We have begun the study of group III with the first member, boron, which is distinctively an acid-forming element. The remaining members of this group, however, are so distinctively base-forming or metallic that they will be studied with the metals.

Having completed our study of the non-metals, or metalloids, as they are termed, we shall now turn to the metals, and with these we shall begin with group I — the alkalies.

CHAPTER XXVI

THE METALS

The metals have certain properties in common which distinguish them from the other elements. With one exception, they are all solids at ordinary temperatures. They are good conductors of heat, and for the most part good conductors of electricity. Their power to conduct electricity, however, varies considerably from metal to metal. Some of the metals, like sodium, potassium, etc., are very active chemically, while others, like platinum, gold, etc., are very resistant to chemical reagents.

The chemistry of the metals is in general much simpler than that of the metalloids. The metals form ions charged with positive electricity, — cations, — and these combine with the anions of acids, forming salts. The cations are generally very much simpler than the anions, consisting usually of single metal atoms charged with positive electricity. There are, however, exceptions to this general statement; a metal may be in combination with other substances, forming part of an anion.

Since when metals react chemically they pass into solution, *i.e.* into the ionic state, the study of the chemistry of the metals is largely the study of the ions which they form. Indeed, we have excellent reason for believing that in order that the metals should react chemically they must be in the ionic state. If this be true, the study of the chemistry of the metals is in reality a study of them in the ionic condition.

We shall now take up the metals one by one, and see what are their peculiarities and the most interesting reactions into which they enter. We shall not, however, take them up at random, since some of the elements are very closely allied in their chemical properties, while others show few and remote relationships. Here, again, we are greatly aided by the Periodic System. In this system the elements which are allied chemically fall into the same groups. While we shall be guided by this system, we shall not hesitate to depart from it in the case of the metals, where relations can be better seen

by doing so, as we have already departed from it in the case of the metalloids.

We shall take up first the alkali metals, consisting of lithium, sodium, potassium, rubidium, and cæsium.

Next in order come the metals of group II. These fall, with respect to their relationships, into two divisions; calcium, strontium, and barium, on the one hand, and beryllium or glucinum, magnesium, zinc, cadmium, and mercury on the other.

When we pass to group III we find that boron has already been studied with the metalloids. The first metal in this group is aluminium. In the same group are the rare elements, scandium, gallium, yttrium, indium, lanthanum, ytterbium, thallium, and samarium.

Passing to iron, we have in this same group nickel, cobalt, manganese, chromium, and the rarer elements, molybdenum, tungsten, and uranium.

Next are taken up copper, silver, and gold, and then lead and tin, the former appearing in group I, the latter in group IV.

Finally, among the noble metals, we have rhodium, ruthenium, palladium, osmium, iridium, and platinum.

CHAPTER XXVII

THE ALKALI METALS

LITHIUM, SODIUM, POTASSIUM, RUBIDIUM, AND CÆSIUM

SODIUM (At. Wt. = 23.05)

The natural order in which to take up the alkali metals would be to start with the one with the lowest atomic weight, lithium, and proceed in the order of increasing atomic weights to cæsium. There are other reasons, however, why this order should not be adopted.

Lithium is a comparatively rare substance occurring only in relatively small quantities.

It is far better, in order to become acquainted with this group, to take up an element which occurs in large quantity, and which can be readily obtained and worked with in the laboratory. Such an element is sodium, the second of the alkalies in the order of increasing atomic weight.

Occurrence of the Element Sodium. — The element sodium is very widely distributed and occurs in combination with other elements in many places in large quantities. On account of its great chemical activity it does not occur in nature in the free condition. Nearly all of the salts of sodium are soluble in water. We should, therefore, expect to find most of the sodium compounds dissolved in the waters of the sea, and such is the fact. When the rocks undergo weathering and set the sodium compounds free, these dissolve readily in water and are swept down to the sea. In this way compounds of sodium, and especially sodium chloride, have been accumulating for ages in the sea, and this is in part the explanation of the saltiness of sea-water. Since practically all of the simple salts of sodium readily dissolve in water, we do not find an accumulation of these salts in regions where there is appreciable rainfall. In certain arid regions, however, one of the most soluble salts of sodium exists in large beds. In Chili large beds of sodium nitrate are found which, from their analogy to potassium nitrate or ordinary saltpetre, are known as *Chili saltpetre.*

Sodium salts exist in great abundance in certain regions where the waters of the sea have evaporated. In the great salt beds of the earth such as those at Stassfurt, the chloride and other compounds of sodium occur. One compound of sodium which has recently come into prominence in connection with the manufacture of aluminium should be mentioned. This is the double fluoride of sodium and aluminium, Na_3AlF_6, occurring in Greenland and known as *cryolite.* Sodium occurs in small quantities practically everywhere and in everything. We have a very sensitive means in the spectroscope of detecting the presence of minute quantities of sodium. When almost any substance is examined in the spectroscope it shows the presence of traces of sodium. Indeed, the atmospheric air always contains sodium. To obtain any substance free from sodium requires the very greatest precautions. The universal presence of sodium seems to be due to its existence in the atmosphere. The chloride is taken up with the water-vapor over the sea, and distributed in minute quantity everywhere.

Preparation of Sodium. — The preparation of the element sodium is of special historical interest.

The compound which we know to-day as sodium hydroxide was supposed for a long time to be an element. When Sir Humphry Davy constructed his enormous voltaic battery in connection with the Royal Institution in London, he tried the action of the current upon a large number of substances, and among these upon fused sodium hydroxide. The result is well known. A metallic substance separated at the cathode, which rose to the surface of the molten hydroxide and took fire spontaneously on coming in contact with the air. The compound nature of sodium hydroxide and the elementary nature of sodium were thus proved beyond question.

Sodium was prepared for a long time by the reduction of the oxide or hydroxide by means of metallic magnesium, or by highly heated carbon: —

$$NaO + Mg = MgO + Na.$$

All of these reduction methods are now abandoned when it is desired to prepare sodium on a large scale. The electrolytic method is used entirely. Considerable sodium has been prepared by the electrolysis of the fused chloride, but these methods involving the use of the chloride are more difficult to carry out than the method employing the fused hydroxide of sodium.

Sodium prepared by electrolysis of the fused hydroxide is not an expensive substance, the price having been reduced immensely by the application of the electrolytic process.

Properties of Metallic Sodium. — Sodium is a soft solid, which, when freshly cut with a knife, has a metallic lustre and a steel-gray color. The surface becomes quickly tarnished, due to the rapidity with which it takes up oxygen from the air or from moisture, forming the oxide or hydroxide. Sodium is a very active substance chemically. It combines readily with moist oxygen, but very slowly, indeed, with dry oxygen. When heated in the presence of oxygen it forms the peroxide NaO. In the presence of water the following reaction takes place: —

$$2\,Na + 2\,H_2O = 2\,NaOH + H_2.$$

The hydrogen, which is liberated when a piece of sodium is thrown upon water, does not take fire if the sodium is allowed to move about over the surface of the water. If the sodium is held in one place, as by throwing it upon a piece of filter-paper upon the water, enough heat is produced to ignite the hydrogen.

With potassium, sodium forms *alloys*, which are liquid at ordinary temperatures. When one part of sodium is fused with four or five parts of potassium the alloy formed is a liquid with metallic appearance, resembling in some respects the amalgams or solutions of the metals in mercury.

Sodium, in the presence of water, forms the hydroxide NaOH, as we have just seen. This, we shall learn, is one of the very strongest bases, and as we would expect combines with all acids. In the light of these facts it is most remarkable that *perfectly dry sodium does not react with perfectly dry sulphuric acid.* When sodium which has been dried with the very greatest precaution is plunged into sulphuric acid from which every trace of water has been removed, it remains suspended in the acid without the least sign of chemical activity. In such experiments unusual precautions must, of course, be taken to remove the last traces of moisture. When there is any moisture present the sodium forms with the water sodium hydroxide, which dissociates, yielding hydroxyl ions, which would then combine with the hydrogen ions resulting from the action of the moisture on the acid. The above is one of the most remarkable facts in the whole field of chemistry, if we try to interpret it in any other light than that furnished by the new physical chemistry. In terms of the theory of electrolytic dissociation and catalysis these facts are just what would be expected, and could have been predicted before they were discovered.

COMPOUNDS OF SODIUM WITH OXYGEN AND HYDROGEN

Sodium Hydride, NaH. — The hydride of sodium, NaH, is formed when sodium is heated to 300° in an atmosphere of hydrogen.

Sodium Peroxide, NaO. — As far as is known with certainty sodium forms only one compound with oxygen. This is the peroxide NaO. It is obtained when sodium is heated in the atmosphere to about 300° to 350°. It is a light-yellow powder, and dissolves readily in water, forming sodium hydroxide and hydrogen dioxide. The reaction would be represented thus: —

$$2\,NaO + 2\,H_2O = 2\,NaOH + H_2O_2.$$

If the temperature is not kept low, a certain amount of oxygen is evolved, and the reaction would be represented thus: —

$$4\,NaO + 2\,H_2O = 4\,NaOH + O_2.$$

Sodium Hydroxide, NaOH. — We have just seen that one method of preparing sodium hydroxide is to treat the oxide with water. Another method, and perhaps the best for preparing a little sodium hydroxide in very pure condition, is to allow water to act on metallic sodium: —

$$2\,Na + 2\,H_2O = 2\,NaOH + H_2.$$

On account of the violence of this reaction it must be carried out with certain precautions. If water were allowed to flow directly upon the metal, the reaction would proceed with such an enormous evolution of heat that an explosion would very probably result. The best way to carry out the reaction is to place a piece of pure sodium in a porcelain dish, and float the dish upon water in a larger vessel — the whole being covered with a bell-jar filled with air from which all carbon dioxide had been removed. The water-vapor comes in contact with the sodium, and the reaction proceeds slowly and without any indication of an explosion or spattering of the alkali. Sodium hydroxide can also be prepared in very pure condition, by treating sodium carbonate with a solution of the hydroxide of any metal which forms an insoluble carbonate; or by treating sodium sulphate with the hydroxide of any metal which forms an insoluble sulphate. If a solution of sodium carbonate is treated with lime water, we have: —

$$Na_2CO_3 + Ca(OH)_2 = CaCO_3 + 2\,NaOH.$$

If a solution of sodium sulphate is treated with a solution of barium hydroxide, we have: —

$$Na_2SO_4 + Ba(OH)_2 = BaSO_4 + 2NaOH.$$

Sodium hydroxide is one of the strongest bases known, as is seen by the following conductivities: —

v	$\mu_v 18^\circ$	a
1	149	79.3 %
10	170	90.4
100	187	99.5
(μ_∞) 500	188	100.0

When brought into the presence of water it dissociates thus: —

$$NaOH = \overset{+}{Na}, \overset{-}{OH}.$$

The basic nature of sodium hydroxide is due to the presence of the hydroxyl ion, as has already been stated. When sodium hydroxide is treated with an acid they react as follows: —

$$\overset{+}{Na}, \overset{-}{OH} + \overset{+}{H}, \overset{-}{Cl} = \overset{+}{Na}, \overset{-}{Cl} + H_2O.$$

This is the typical reaction between an acid and a base, an example of which we have already met with in the case of ammonium hydroxide. The cation of the base and the anion of the acid remain in the same condition after neutralization as before. The anion of the base, hydroxyl, and the cation of the acid, hydrogen, unite and form water, and this is all that takes place in the process of neutralization. To obtain the salt of sodium it is only necessary to evaporate the solution after neutralization. In the above example, when the water is removed, the sodium and chlorine ions unite and form the salt sodium chloride.

The Chemistry of Sodium the Chemistry of the Sodium Ion. — The chemistry of the element sodium is not the chemistry of the atom or molecule of sodium, since there is every reason for believing that these are practically inert. Perfectly dry sodium contains an abundance of atoms or molecules, and yet will not react chemically. We have already seen that dry sodium, free from every trace of moisture, will not act upon perfectly dry sulphuric acid. Dry sodium will not act on dry chlorine gas, but will remain molten in contact with the gas without having even its surface tarnished. There is good reason for believing that dry sodium will not act upon dry oxygen, and thus

it goes through the list of chemical reactions which are characteristic of this element.

It may be said that the presence of traces of moisture acts catalytically, effecting the action without taking part in it. This is, of course, a mere assumption and does not explain anything. It seems far more probable that the presence of even traces of water causes a slight dissociation of the substances, and as soon as the ions thus formed are used up more ions are formed, and this may continue until the reaction proceeds practically to the end.

On the other hand, wherever we have sodium ions present we have the reactions which are characteristic of this element. Some of these reactions, together with their products, we shall now study.

Compounds of Sodium with the Halogens. — The strong base, sodium hydroxide, combines with the strong halogen acids, as we would expect, forming salts. Or, more accurately stated, the cation sodium combines with the halogen anion, forming the sodium salt of the halogen.

Sodium Chloride is found in great abundance in sea-water, which, on the average, contains about 2.7 per cent of the salt. The amount of sodium chloride in sea-water, however, varies greatly from one locality to another. In tropical regions, where the evaporation of the water is relatively rapid, the concentration may be as much as 3.5 to 3.8 per cent. Where large bodies of fresh water pour into the sea the percentage of sodium chloride may be reduced below unity. In certain isolated bodies of water, as the Dead Sea, the amount of sodium chloride may be more than 20 per cent. It also occurs in the solid form in a number of the great salt-deposits, and especially in those of Salzburg, Germany. This salt is also obtained from sea-water by evaporation. The water is allowed to flow into shallow pools, and be evaporated by the heat of the sun. After this has been repeated a sufficient number of times the salt is removed and purified.

Sodium chloride is also obtained directly in the solid form from many of the great salt beds. Sodium chloride crystallizes in characteristic, hopper-shaped cubes. These cubes are not completely filled out, but are hollow in the centre. It melts at about 780°, *decrepitating* or flying to pieces when heated. The salt is nearly as soluble in cold water as in hot, one part of water dissolving 0.36 parts of sodium chloride. Sodium chloride is present in considerable quantity in the animal body, and is especially sought for by herbivorous animals.

On account of its abundance and cheapness, sodium chloride is of great importance as a source of both chlorine and sodium. When

electrolyzed, either in the molten condition or in concentrated solution, chlorine is set free at the anode. When treated with a strong non-volatile acid such as sulphuric, hydrochloric acid is evolved. It is readily transformed into other compounds of sodium, including the hydroxide, and is thus the source of such compounds as well as of the element itself.

Purification of Sodium Chloride. — Since sodium chloride is just about as soluble in cold as in hot water, the ordinary method of purification, based upon fractional crystallization, cannot be very successfully applied in this case. A method of purification which involves a general principle can, however, be applied.

If to a *saturated solution* of sodium chloride either *sodium ions or chlorine ions* are added, some of the sodium chloride will be precipitated. The most convenient method of adding chlorine ions to a solution without increasing the amount of the solvent present, is to pass into the solution hydrochloric acid gas. If hydrochloric acid gas is passed into a saturated solution of sodium chloride, some of the latter compound is precipitated, and the amount precipitated depends upon the amount of acid which is run into the solution.

We can test the first part of the statement, that an addition of sodium ions will cause a precipitation of the sodium chloride with which the solution is saturated, by adding to such a solution some solid, sodium salt, such as the nitrate. The sodium nitrate will dissolve in the saturated solution of the chloride, and dissociate into sodium ions and the nitro-ion $\bar{N}O_3$. A part of the sodium chloride in the saturated solution will be precipitated in solid form.

There is a general principle involved here, deduced by the German physical chemist, Nernst, from the law of the action of mass, with which we have already become familiar. In any saturated solution the *product of the number of cations times the number of anions is a constant.* This condition always obtains for a saturated solution, and may be known as the *law of saturation.*

If to a saturated solution of sodium chloride we add either common ion, sodium or chlorine, the solution will still be saturated with sodium and chlorine ions, and only saturated.

In order that the relation —

$$\text{cations} \times \text{anions} = \text{constant}$$

should obtain, if we increase the number of cations, the number of anions present must diminish; or if we increase the number of anions, the number of cations present must decrease. The way in which this can occur is for a certain number of cations to combine with an

equal number of anions, and form molecules of the salt. The solution is, however, saturated with respect to the salt, and as quickly as any of the salt is formed by a combination of its ions it is precipitated. It is obvious from the above equation that the larger the excess of cations or anions added to the solution, the greater the amount of the salt which will be precipitated.

This principle is taken up here because it is an excellent means of purifying chlorides. Hydrochloric acid being volatile, it can readily be conducted into a saturated solution of any chloride, when some of the chloride with which the solution is saturated will be precipitated, and only this substance. If the nitro-ions $\bar{NO_3}$ could be added to a saturated solution of a nitrate, or the sulphuric ions $\bar{\bar{SO_4}}$ to a saturated solution of a sulphate, we should have a part of the original nitrate or sulphate precipitated.

The physical chemical importance of this law of saturation is very great indeed, since it has led to a method of measuring electrolytic dissociation, which, however, it would lead us too far to discuss.

Sodium forms with chlorine a *subchloride*, Na_2Cl. This is obtained by heating sodium chloride with metallic sodium at a high temperature. It is deep-blue in color.

Sodium Bromide (NaBr) and Sodium Iodide (NaI). — These salts resemble sodium chloride so closely that a detailed study of them is not necessary. Certain phenomena connected with their formation from aqueous solution and with their solubility are of interest.

If these salts are crystallized from hot, aqueous solutions, they come down in the anhydrous condition. If the temperature at which they crystallize is below 30°, they come down with two molecules of water of crystallization. If the salts containing water of crystallization are heated, the bromide to 50°, the iodide to 67°, they form the corresponding anhydrous salts and saturated solutions of these salts.

If we study the solubility of these two salts with rise in temperature and plot the results as curves, the abscissas being temperatures and the ordinates parts of salts in one hundred parts of water, the curves would have the form shown in Fig. 33.

The curves show that the salt with water of crystallization increases in solubility with rise in temperature until the transition point, where the two curves intersect, is reached. After this temperature is passed the solubility of sodium bromide remains nearly constant as the temperature rises, while the solubility of sodium iodide increases with rise in temperature, but much more slowly

than the solubility of the iodide with water of crystallization. The curves are all plotted beyond the transition-points as dotted lines. This means that we may have either phase extending into the region of the other in a metastable condition.

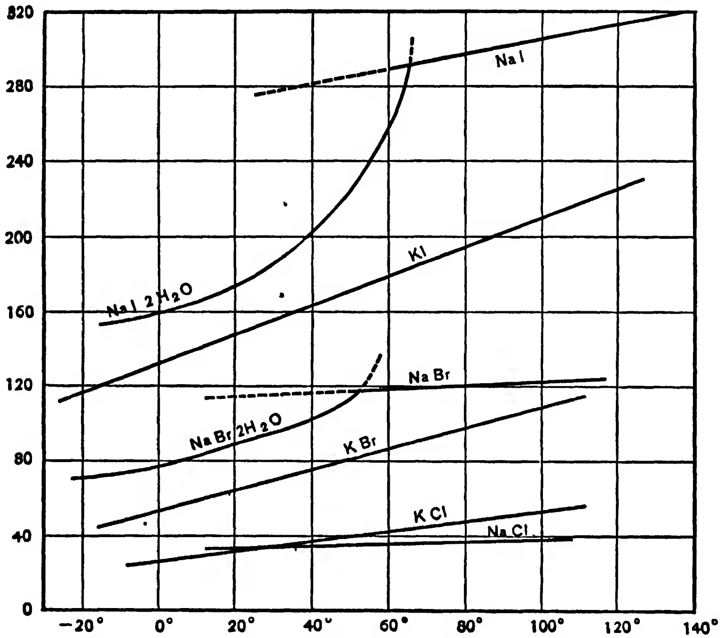


FIG. 33.

Ostwald has shown that the merest trace of the phase which is stable under the conditions, is sufficient to cause the metastable to pass over into the stable condition.

Sodium Hypochlorite ($NaOCl$), Chlorate ($NaClO_3$), and Bromate ($NaBrO_3$). — Sodium forms salts with the oxygen acids of the halogens, which are well-defined, stable substances, but for the most part are without special chemical interest.

The *hypochlorite* is used now to some extent as a disinfectant, and in bleaching.

The *chlorate* is formed by the action of chlorine on sodium hydroxide: —

$$6\,NaOH + 3\,Cl_2 = 5\,NaCl + NaClO_3 + 3\,H_2O.$$

Sodium chlorate, unlike potassium chlorate, is quite soluble in water, and is, therefore, much more difficult than potassium chlorate to separate from the corresponding chloride. It crystallizes in

cubes, and has one property of more than the average interest. When a beam of polarized light is passed through the crystal, the plane of the beam is turned around an axis. As we say, it has the power to rotate the plane of polarization. There are many substances known which have this power, but they are mainly in the field of organic chemistry.

Sodium bromate is prepared in a manner which is analogous to the preparation of the chlorate, *i.e.* by the action of bromine on sodium hydroxide.

Sodium Triazoate (NaN_3) and Sodium Amide ($NaNH_2$). — The sodium salt of triazoic or hydrazoic acid is well known. It is formed by the action of the hydroxide or carbonate of sodium upon hydrazoic or triazoic acid. The salt crystallizes in cubes and is remarkable for its composition, consisting of a sodium atom in combination with three nitrogen atoms. As we would expect, such a compound is unstable, and in the dry condition easily explodes.

Sodium amide, $NaNH_2$, is formed when perfectly dry ammonia gas is passed over heated sodium. The action is as follows: —

$$2\,NH_3 + 2\,Na = 2\,NH_2Na + H_2,$$

sodium replacing one hydrogen atom in ammonia and combining with the residue NH_2. When sodium amide is treated with nitrous oxide the sodium salt of hydrazoic acid is formed: —

$$2\,NaNH_2 + N_2O = NaOH + NH_3 + NaN_3.$$

When the sodium salt is treated with a strong acid, triazoic acid is formed, and this is the simplest means of preparing this substance.

Sodium Nitrate, $NaNO_3$. — Sodium nitrate is called Chili saltpetre because it is found in a certain, rainless district between Chili and Peru, and since it is the sodium analogue of potassium nitrate or ordinary saltpetre. It is extremely soluble in water, and, therefore, could not exist in the solid condition in regions where there is appreciable rainfall. To give an idea as to its extreme solubility a few data are added. At the following temperatures, one part of water dissolves so many parts of sodium nitrate: —

Temperature	$NaNO_3$, Parts dissolved by one Part Water
0°	0.73
40°	1.02
80°	1.50
110°	2.00

Sodium nitrate, being so readily soluble in water, forms in aqueous solution, a solution of NO_3 ions. These are taken up by the plants and, if not too concentrated, are among the most valuable fertilizing agents. Considerable quantities of sodium nitrate are added directly to the soils as a fertilizer, where quick results are desired. On account of its great solubility, it is quickly accessible to plants, and for such products as are common to the garden it is one of the very best fertilizers.

Sodium nitrate cannot be used in making gun-powder in the place of potassium nitrate, since it absorbs water from the air, or is *deliquescent*, as we say. It is, however, extensively used in the preparation of potassium nitrate. It is also extensively used in the preparation of ammonium nitrate, free nitric acid, and of sodium nitrite.

Sodium Nitrite, $NaNO_2$.— The nitrites can be obtained in general by heating the nitrates. Unless the heating is very carefully done, and even then, there is considerable decomposition of the nitrite. The best method of preparing sodium nitrite is by fusing the nitrate with some mild reducing agent such as metallic lead: —

$$NaNO_3 + Pb = PbO + NaNO_2.$$

Sodium nitrite is extensively used in the preparation of artificial dyestuffs. When treated with an acid, sodium nitrite breaks down thus: —

$$2\,NaNO_2 + H_2SO_4 = Na_2SO_4 + 2\,HNO_2.$$

The nitrous acid, however, undergoes decomposition: —

$$2\,HNO_2 = H_2O + N_2O_3,$$

and the gas N_2O_3 is useful in effecting certain reactions in organic chemistry.

Sodium Hydrosulphide (NaHS) and Sodium Sulphides (Na_2S to Na_2S_5). — Sodium hydrosulphide is formed when a solution of sodium hydroxide is saturated with hydrogen sulphide gas: —

$$NaOH + H_2S = H_2O + NaSH.$$

If to a solution of sodium hydrosulphide an equivalent of sodium hydroxide is added, the sulphide of sodium is formed: —

$$NaHS + NaOH = Na_2S + H_2O.$$

There are a number of polysulphides of sodium varying in composition from Na_2S_2 to Na_2S_5. These are prepared by fusing sulphur

with sodium carbonate. When treated with an acid they liberate hydrogen sulphide and free sulphur.

$$Na_2S_3 + 2\,HCl = 2\,NaCl + H_2S + 2\,S.$$

Sodium Sulphite, $Na_2SO_3 . 7\,H_2O$. — When sulphur dioxide is conducted into a solution of sodium hydroxide, sodium sulphite is formed:—

$$2\,NaOH + SO_2 = Na_2SO_3 + H_2O.$$

Sulphurous acid also forms the acid salt $NaHSO_3$. Sodium sulphite is oxidized to some extent to the sulphate by the oxygen of the air.

It is *hydrolytically dissociated* by water, as is shown by the alkaline reaction of its aqueous solution: —

$$Na_2SO_3 + H_2O = \overset{+}{Na}, \overset{-}{OH} + \overset{+}{Na}, H\overset{-}{SO_3}.$$

The hydroxyl ion gives its characteristic alkaline reaction.

Sodium Sulphate, $Na_2SO_4 . 10\,H_2O$. — Sodium sulphate, called from its discoverer, *Glauber's salt*, exists in certain mineral waters as those of Carlsbad, and occurs as the mineral *thenardite*. It is formed in a large number of reactions. When sulphuric acid is neutralized with sodium hydroxide we have:—

$$2\,NaOH + H_2SO_4 = 2\,H_2O + Na_2SO_4.$$

When sodium chloride is treated with sulphuric acid, sodium sulphate is formed, not because sulphuric acid is as strong as hydrochloric, but because the latter is volatile:—

$$2\,NaCl + H_2SO_4 = 2\,HCl + Na_2SO_4.$$

A similar reaction takes place with sodium nitrate, nitric acid being volatile: —

$$2\,NaNO_3 + H_2SO_4 = 2\,HNO_3 + Na_2SO_4.$$

Similarly, with sodium carbonate: —

$$Na_2CO_3 + H_2SO_4 = H_2O + CO_2 + Na_2SO_4,$$

and, in general, whenever a salt of a volatile acid is treated with sulphuric acid and the temperature raised, the volatile acid escapes and the sulphate remains behind.

Sulphates can also be formed by *double decomposition or metathesis*. Thus, when a solution of sodium carbonate is treated with a solution of a sulphate of a metal whose carbonate is insoluble, an exchange of ions takes place. Take as an example sodium carbonate and zinc sulphate: —

$$\overset{+}{Na}, \overset{+}{Na}, \overset{=}{CO_3} + \overset{++}{Zn}, \overset{=}{SO_4} = \overset{+}{Na}, \overset{+}{Na}, \overset{=}{SO_4} + ZnCO_3.$$

The zinc carbonate is insoluble and can be filtered off, the sodium sulphate remaining in the solution in the ionic condition. When the solution is evaporated the ions combine and sodium sulphate is obtained. When sodium sulphate with ten molecules of water of crystallization is exposed to the air, it loses part of its water at ordinary temperatures. Such salts are termed *efflorescent.*

Sodium sulphate is used as a purgative. It is a stage, as we shall soon see, in the manufacture of sodium carbonate. When mixed with concentrated hydrochloric acid it forms a good refrigerating agent.

Solutions of sodium sulphate in water present a number of points of interest. The facts are these: If sodium sulphate is allowed to crystallize from its solution above 33°, the anhydrous salt Na_2SO_4 separates. The solubility of the anhydrous salt is shown in curve 1, Fig. 34, the solubility decreasing with rise in temperature. This anhydrous salt can exist below 32°, if there is not more than 0.000001 milligram of the hydrated salt present. The solubility of this salt has been studied considerably below 32°, and the results are shown in the dotted extension of curve 1. If there is present even the smallest trace of the salt with ten molecules of water, the anhydrous salt cannot exist below 32°.

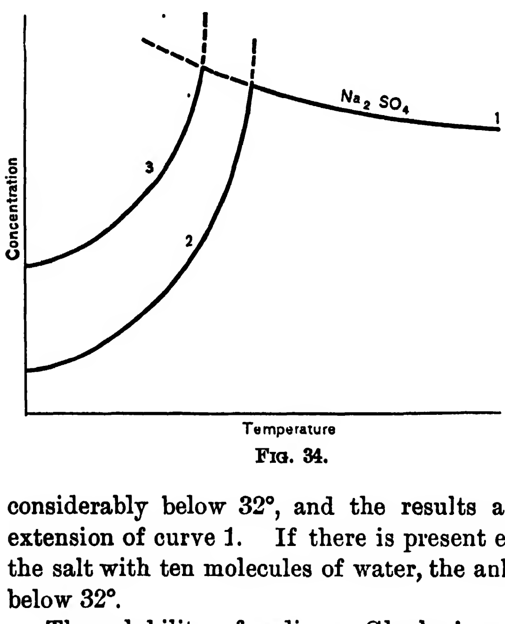


FIG. 34.

The solubility of ordinary Glauber's salt with ten molecules of water of crystallization, has been studied at different temperatures, and the results are plotted in curve 2. Unlike the anhydrous salt the solubility of the hydrated salt decreases with decrease in temperature, and this very rapidly. At 32° the two curves intersect, the point of intersection representing equilibrium between the anhydrous salt, the salt with ten molecules of water of crystallization, and the saturated solution.

If a supersaturated solution of Glauber's salt is cooled to 5°, another solid phase separates, having the composition $Na_2SO_4 . 7\,H_2O$.

The solubility of this salt has been studied and the results are plotted in curve 3; its solubility is greater than that of the Glauber's salt.

Acid Sodium Sulphate ($NaHSO_4$) and Sodium Pyrosulphate ($Na_2S_2O_7$). — Acid sodium sulphate is formed by the action of sulphuric acid on salts of sodium with volatile acids: —

$$NaCl + H_2SO_4 = NaHSO_4 + HCl,$$
$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3.$$

Also by the action of sulphuric acid on the neutral sulphate: —

$$Na_2SO_4 + H_2SO_4 = 2\,NaHSO_4.$$

When carefully heated in a vacuum to 300° it loses water and forms the pyrosulphate: —

$$2\,NaHSO_4 = H_2O + Na_2S_2O_7.$$

When the pyrosulphate is heated still higher, and especially when in contact with the oxides of certain metals, the following decomposition takes place: —

$$Na_2S_2O_7 = Na_2SO_4 + SO_3.$$

Sulphur trioxide is a powerful reagent, attacking most substances with which it comes in contact. The acid sulphates are, therefore, useful as reagents, especially in the fused condition.

Sodium Thiosulphate, $Na_2S_2O_3.5\,H_2O$. — This salt is frequently referred to as sodium hyposulphite, or in commerce simply as "hypo." It is prepared by dissolving sulphur in a solution of sodium sulphite: —

$$Na_2SO_3 + S = Na_2S_2O_3.$$

Solutions of this salt dissolve silver chloride and bromide, and it is, therefore, used to remove these substances from the photographic plate after the plate has been exposed to the light. If the unchanged portions of these salts were not removed, the plate would still be sensitive to light, and a slight exposure would ruin the photograph. It is known in photography as a "fixing" agent. As has already been mentioned this salt is used to remove the last traces of chlorine from fabric which has been bleached by chlorine. In this capacity it is known as "antichlor." The products of this reaction are hydrochloric acid, sulphuric acid, sodium chloride, and sodium sulphate: —

$$Na_2S_2O_3 + 4\,Cl_2 + 5\,H_2O = 7\,HCl + NaCl + H_2SO_4 + NaHSO_4.$$

Although bromine reacts with the thiosulphate in a similar manner, iodine behaves very differently. The thiosulphate is converted by iodine into the tetrathionate, and sodium iodide is formed: —

$$2\,Na_2S_2O_3 + 2\,I = Na_2S_4O_6 + 2\,NaI.$$

A standard solution of sodium thiosulphate, containing a known amount of the salt in a given volume of the solution, is used to determine the amount of free iodine present under any given conditions. The iodine is transformed into sodium iodide, which is colorless. It is, therefore, a very simple matter to determine when the iodine is all transformed into the iodide.

Sodium Carbonate, $Na_2CO_3.10\,H_2O$. — The salt with ten molecules of water crystallizes from a solution allowed to cool on the air. If a hot, concentrated solution is allowed to cool in such a way as to be protected from any sodium carbonate which may be in the air, the salt $Na_2CO_3.7\,H_2O$ separates. There are two varieties of the septahydrate which have different crystalline forms, and which differ considerably in their solubility in water.

If the saturated solution of sodium carbonate is boiled to crystallization, the monohydrate $Na_2CO_3.H_2O$ separates. The salt with ten molecules of water passes into the salt with one molecule of water at 34°. This is the transition point between these two phases. The monohydrate is less soluble the higher the temperature, and in this respect is analogous to anhydrous sodium sulphate.

When any one of the hydrates of sodium carbonate is heated to a sufficiently high temperature, it gives up water step by step, and passes over into the anhydrous salt. Indeed, the salt with ten molecules of water loses a part of its water at ordinary temperatures — is *efflorescent.*

Sodium carbonate was formerly obtained from the ashes of sea-plants, but on account of its great importance, especially in connection with the manufacture of glass and soap, methods have been devised for manufacturing it.

The *Le Blanc Method* of preparing sodium carbonate was used almost exclusively until quite recently, when another method was devised which bids fair to supplant it. In the Le Blanc method the sodium chloride is converted into the sulphate by means of sulphuric acid. The sulphate is reduced to the sulphide by means of highly heated carbon. The third and last process is to heat sodium sulphide with calcium carbonate, when, at a sufficiently high temperature, calcium sulphide and sodium carbonate are formed. The reactions expressing these three transformations are: —

$$\text{I.} \qquad 2\,NaCl + H_2SO_4 = 2\,HCl + Na_2SO_4,$$
$$\text{II.} \qquad Na_2SO_4 + 4\,C = 4\,CO + Na_2S,$$
$$\text{III.} \qquad Na_2S + CaCO_3 = CaS + Na_2CO_3.$$

It is not difficult to separate the sodium carbonate from the calcium sulphide, since the latter is difficultly soluble in water, while sodium carbonate is readily soluble.

The sodium carbonate thus obtained is impure and is known as soda ash or crude soda. It is purified by crystallization from water.

The sulphur is obtained from the calcium sulphide by means of carbon dioxide. When this is conducted into the moist, calcium sulphide, calcium carbonate and hydrogen sulphide are formed. The hydrogen sulphide is then burned by means of the oxygen of the air and there is formed sulphur, or sulphur dioxide, which can readily be transformed into the trioxide, and this with water into sulphuric acid.

The Solvay or Ammonia Process is based upon the fact that acid sodium carbonate is much less soluble in water than acid ammonium carbonate. Ammonia and sodium chloride are dissolved in water, and carbon dioxide passed into the mixture. Under these conditions acid sodium carbonate, on account of its small solubility, separates from the solution. The reactions may be represented thus: —

$$NH_3 + H_2O + CO_2 = NH_4HCO_3,$$
$$NH_4HCO_3 + NaCl = NH_4Cl + HNaCO_3.$$

The acid sodium carbonate when heated forms the normal carbonate, carbon dioxide, and water: —

$$2\,HNaCO_3 = H_2O + CO_2 + Na_2CO_3.$$

The carbon dioxide is conducted into more ammonia in the presence of sodium chloride, and the process is thus a continuous one.

Acid Sodium Carbonates, $NaHCO_3$ and $Na_3H(CO_3)_2, 2\,H_2O$. — Primary sodium carbonate, or acid sodium carbonate, or the "bicarbonate of soda," is formed by the action of carbon dioxide on the normal carbonate: —

$$Na_2CO_3 + CO_2 + H_2O = 2\,NaHCO_3.$$

It is also formed, as we have just seen, in the preparation of normal sodium carbonate by the ammonia process. When acid ammonium carbonate, formed by the action of carbon dioxide on ammonia, is treated with sodium chloride, acid sodium carbonate is formed: —

$$NH_4HCO_3 + NaCl = NaHCO_3 + NH_4Cl.$$

When primary sodium carbonate is boiled with water, it loses carbon dioxide and dissolves as the normal carbonate. When the solution is evaporated quickly the sesquicarbonate $Na_2CO_3, NaHCO_3 . 2 H_2O$ separates.

Hydrolysis of the Carbonates. — The aqueous solution of normal sodium carbonate has a strongly alkaline reaction. Indeed, the primary or acid carbonate has a weakly alkaline reaction. This is due to the presence of hydroxyl ions in the aqueous solutions of the carbonates. The carbonates are salts of the very weak, carbonic acid, and like all salts of weak acids are hydrolyzed to a greater or less extent by water:—

$$Na_2CO_3 + H_2O = \overset{+}{Na}, \overset{-}{O}H + \overset{+}{Na}, H\overset{-}{C}O_3.$$

Even the acid carbonate is hydrolyzed to a sufficient extent to show an alkaline reaction.

All carbonates which are soluble in water are hydrolyzed to a sufficient extent to show an alkaline reaction.

The Phosphates of Sodium. — Since phosphoric acid is tribasic, there are three sodium salts of this acid possible, and all are known. The *secondary sodium phosphate*, Na_2HPO_4, is by far the best known, and is always meant when the term sodium phosphate is used without qualification. It contains twelve molecules of water of crystallization. It is a beautifully crystalline compound, containing, as ordinarily formed, twelve molecules of water of crystallization. When crystallized above 35°, it comes down with seven molecules of water.

Its aqueous solution is slightly alkaline, due to the fact that the phosphoric acid is a weak acid, and it is slightly hydrolyzed by water: —

$$Na_2HPO_4 + H_2O = \overset{+}{Na}, \overset{-}{O}H + \overset{+}{Na}, H_2\overset{-}{P}O_4.$$

When carbon dioxide is conducted into a solution of disodium phosphate, we have a liquid with both acid and alkaline reaction, — it colors blue litmus red, and red litmus blue. Such reactions are known as *amphoteric*.

When disodium phosphate is treated with one equivalent of phosphoric acid, the *monosodium phosphate* H_2NaPO_4 is formed: —

$$Na_2HPO_4 + H_3PO_4 = 2 NaH_2PO_4.$$

The monosodium phosphate crystallizes in two forms, each containing one molecule of water of crystallization.

If, on the other hand, one equivalent of sodium hydroxide is added

to one equivalent of disodium phosphate, the *trisodium phosphate* is formed: —

$$Na_2HPO_4 + NaOH = Na_3PO_4 + H_2O.$$

The trisodium phosphate crystallizes with twelve molecules of water, $Na_3PO_4 . 12\,H_2O$. When this salt is dissolved in water the solution shows a strongly alkaline reaction, due to the marked hydrolysis of this salt by water: —

$$Na_3PO_4 + H_2O = \overset{+}{Na}, \overset{-}{OH} + \overset{+}{Na}, \overset{+}{Na}, H\overset{=}{PO_4}.$$

When a primary phosphate is heated it loses water, forming a *metaphosphate*: —

$$NaH_2PO_4 = H_2O + NaPO_3.$$

When disodium phosphate is heated, a *pyrophosphate* is formed: —

$$2\,HNa_2PO_4 = H_2O + Na_4P_2O_7.$$

This crystallizes with ten molecules of water: —

$$Na_4P_2O_7 . 10\,H_2O.$$

The metaphosphate of sodium is used like borax in qualitative analysis. It readily fuses, forming a clear liquid, and this liquid dissolves the oxides of many metals, forming glass-like masses, which have characteristic colors. By means of this reaction, small quantities of many metals can be detected. The metaphosphate is fused in a Bunsen burner, or a blowpipe, in the loop of a platinum wire, and a small part of the substance to be analyzed is added to the fused metaphosphate. The color of the bead when hot and when cold is observed, and the metal thus identified.

Sodium Ammonium Phosphate, $NaNH_4HPO_4.4\,H_2O$. — The double phosphate of sodium and ammonium is also of importance in analysis. It is really a triple phosphate of sodium, ammonium, and hydrogen. It is formed by bringing together, in solution, disodium phosphate and ammonium chloride: —

$$Na_2HPO_4 + NH_4Cl = NaCl + NH_4NaHPO_4.$$

When heated it decomposes into ammonia, water, and sodium metaphosphate: —

$$NH_4NaHPO_4 = NH_3 + H_2O + NaPO_3.$$

This salt is known as *microcosmic salt*, and is generally used as the means of preparing sodium metaphosphate. When a small piece of microcosmic salt is heated in the loop of a platinum wire, the above

decomposition takes place, and sodium metaphosphate results. This dissolves metal oxides as already described.

Sodium Borate or Tetraborate, $Na_2B_4O_7 . 10\,H_2O$. — Borax is not the salt of normal boric acid, H_3BO_3, but of a polyboric acid derived from the normal acid by loss of water. When four molecules of boric acid lose five molecules of water, the acid from which borax is formed results: —

$$4\,H_3BO_3 = 5\,H_2O + H_2B_4O_7.$$

Borax, or sodium tetraborate, is found in a few localities in certain lakes, notably in the western part of the United States and in Asia. It is formed when boric acid is neutralized with sodium carbonate: —

$$4\,H_3BO_3 + Na_2CO_3 = Na_2B_4O_7 + 6\,H_2O + CO_2.$$

When borax crystallizes from aqueous solution below 56°, it comes down with ten molecules of water of crystallization — $Na_2B_4O_7 . 10\,H_2O$. When it crystallizes from a solution above 56°, it contains only five molecules of water, $Na_2B_4O_7 . 5\,H_2O$. This temperature (56°) is then the transition temperature between the two hydrates of borax. The former, from its prismatic form, is known as "prismatic" borax, the latter as "octahedral" borax. When borax is heated to a higher temperature, it gives off all of its water and then fuses to a clear liquid. This liquid, as we have already stated, has the power to dissolve oxides of certain metals, and form with them vitreous masses with characteristic colors. The "borax bead," like the microcosmic bead, is, therefore, very useful in qualitative chemistry.

On account of this property of dissolving metal oxides borax is frequently used as a *flux*. It is used for the same reason to clean two metal surfaces which it is desirable to *solder* together. These usually become covered with a layer of oxide when the metal is heated, and the solder, or easily fusible alloy, will not adhere to the surfaces while the oxide is present. When a little borax is added, it removes at the elevated temperature the oxides already formed, and at the same time protects the hot metal surfaces from the oxygen of the air. Borax is used only when hard solder, which is an alloy of zinc, copper, and silver, is employed. When ordinary soft solder is used, it is better to moisten the surfaces with a solution of zinc chloride to which a little hydrochloric acid has been added.

Sodium Silicate, Na_2SiO_3.—It has already been mentioned that the silicates of the alkalies are soluble in water. When finely powdered

sand is fused with sodium hydroxide or sodium carbonate, sodium silicate is formed: —

$$SiO_2 + 2\,NaOH = Na_2SiO_3 + H_2O.$$

Sodium silicate is known as *sodium waterglass.* It is readily soluble in water, depositing a vitreous coating when the water is allowed to evaporate.

Sodium Pyroantimoniate, $Na_2H_2Sb_2O_7$. — This salt is of special interest, because it is one of the few salts of sodium which is difficultly soluble in water. It requires about 350 parts of water to dissolve this salt. When a solution of potassium pyroantimoniate is added to a solution of a sodium salt, sodium pyroantimoniate is precipitated: —

$$K_2H_2Sb_2O_7 + 2\,NaCl = 2\,KCl + Na_2H_2Sb_2O_7.$$

The sodium salt of sulphantimonic acid — Na_3SbS_4 — known as *Schlippe's salt,* has already been referred to.

Sodium Acetate, $CH_3COONa.3\,H_2O$. — One or two compounds of sodium with organic acids will be referred to. Sodium acetate is formed by neutralizing acetic acid with sodium hydroxide, and evaporating the solution to crystallization. Sodium acetate is very soluble in water, one part of salt dissolving at 50° in 1.7 parts of water.

Sodium acetate is used extensively in analysis. When an acid is added to sodium acetate, *i.e.* when free hydrogen ions are added, acetic acid is formed. Acetic acid, however, being a very weak acid, is only slightly dissociated in aqueous solution. When free hydrogen ions are added to sodium acetate the following reaction takes place: —

$$\overset{+}{H}, \overset{-}{Cl} + \overset{+}{Na}, CH_3\overset{-}{C}OO = \overset{+}{Na}, \overset{-}{Cl} + CH_3COOH.$$

The hydrogen ions are thus removed from the field of action, and are prevented from dissolving substances which are soluble in water containing a large number of these ions.

Sodium Cyanide, NaCN. — The sodium compound of hydrocyanic acid presents interesting solubility relations. When it crystallizes from a solution whose temperature is above 33°, the anhydrous salt separates. Below this temperature the salt crystallizes with one or more molecules of water, depending upon conditions.

Spectrum of Sodium. — Sodium is readily recognized by means of the color which it imparts to the flame. If a platinum wire containing a sodium salt is introduced into the colorless flame of a Bunsen burner, the flame becomes immediately colored bright yellow. If

such a flame is examined by means of the spectroscope it will be found to contain an intensely bright line in the yellow. This is known as the sodium line, or in spectroscopy as the D line.

The almost universal presence of sodium is shown by means of the spectroscope. The D line appears under almost all conditions, unless very special precautions are taken to exclude it. Whenever any flame is examined by the spectroscope under ordinary conditions the D line appears, and is used as a standard with which to compare other spectroscopic lines.

CHAPTER XXVIII

POTASSIUM (At. Wt. = 39.15)

Occurrence and Preparation.—Potassium like sodium does not occur in nature in the free condition, and for the same reason, viz. the great chemical activity of the substance. Although the salts of potassium, like those of sodium, are soluble in water, they are not carried down to the sea in anything like the same relative quantity.

This is due to the fact that plants have the power of taking up potassium ions in large quantities and building them up in their tissues. They exercise selective absorption for potassium ions, allowing the sodium to be carried on by the same waters from which they remove the potassium. When such plants are burned the potassium salts remain behind in the ashes. Potassium occurs in large quantity in the ashes of certain kinds of wood, as is well known, and can be easily leached out of the ashes by means of water which is allowed to trickle through them. The *lye* thus obtained contains a large amount of potassium hydroxide.

Potassium also occurs in many of the more common rocks and minerals in the form of silicates. Ordinary *feldspar* is the double silicate of potassium and aluminium. When these are decomposed by weathering the potassium salts are set free and become available for plants.

Potassium salts also occur in the great salt beds, especially in those of Stassfurt, in Germany. The chloride is known as *sylvite*, the nitrate as *saltpetre*, and the sulphate, when in combination with other metallic sulphates, as *alums*. *Carnallite* contains also magnesium.

The preparation of the element potassium is of the same historical interest as the preparation of sodium. Potassium hydroxide like sodium hydroxide was regarded as elementary until Sir Humphry Davy, in 1807, electrolyzed fused protassium hydroxide. This compound was decomposed by the current, yielding metallic potassium at the cathode and oxygen at the anode. The metal rose to the surface of the fused hydroxide, and took fire spontaneously on coming in contact with the air.

Potassium was next prepared by reducing potassium carbonate with carbon: —

$$K_2CO_3 + 2\,C = 2\,K + 3\,CO.$$

Potassium was prepared later by reducing the sulphide or hydroxide with highly heated metals, such as magnesium, aluminium, iron, etc.: —

$$K_2S + Fe = FeS + K_2.$$

$$2\,KOH + 2\,Mg = 2\,K + 2\,MgO + H_2.$$

All of these methods have now been abandoned in favor of the electrolytic. Metallic potassium is now prepared by electrolyzing the chloride, or hydroxide. The high fusing-point of the chloride is objectionable, since at these high temperatures metallic potassium acts on potassium chloride, forming the subchloride. To lower the temperature at which potassium chloride can be kept in the molten condition, it is mixed with calcium chloride.

Properties of Potassium. — Potassium is characterized by its great chemical activity, being even more active than sodium. When a small piece of potassium is thrown upon water it decomposes it in the same manner as sodium, yielding potassium hydroxide and setting hydrogen free: —

$$2\,H_2O + 2\,K = 2\,KOH + H_2.$$

The action in the case of potassium is, however, so vigorous that even when the metal is allowed to move around over the surface of the water, enough heat is generated to ignite the hydrogen.

Potassium combines with the oxygen of the air with the greatest readiness, and, therefore, cannot be kept in contact with the air. Like sodium it is preserved under petroleum.

On account of its combining so readily with oxygen it is an excellent reducing agent, setting metals such as aluminium free from their oxides.

Potassium does not combine with dry oxygen, but combines with the greatest vigor if the merest trace of moisture is admitted. This is another example of the wonderful influence exerted by water on chemical activity.

Potassium is of the same general appearance as sodium. A fresh surface has a light-steel color, but is very quickly tarnished by contact with the air. It melts at 62°.5, and boils at 670°.

The molecular weight of metallic potassium dissolved in mercury, as determined by the lowering of the freezing-point of the mercury, is practically identical with the atomic weight.

Potassium Hydride, KH. — When potassium is heated in an atmosphere of hydrogen, the two elements combine, forming the hydride of potassium. The combination takes place rapidly at 350°. If potassium hydride is heated a little above 400°, it dissociates into potassium and hydrogen.

Potassium Peroxide, KO_2. — The only compound which potassium is known to form with oxygen is the dioxide. It is obtained by heating potassium in a current of dry oxygen. It is an orange-colored powder, melting at 280°. In contact with water it forms potassium hydroxide and hydrogen dioxide: —

$$2\,KO_2 + 2\,H_2O = 2\,KOH + H_2O_2 + O_2.$$

Potassium Hydroxide, KOH. — When metallic potassium is thrown upon water, potassium hydroxide is formed, as we have seen.

It is also formed when the peroxide is dissolved in water.

It can be readily formed by treating potassium carbonate with the hydroxide of a metal whose carbonate is insoluble, say calcium hydroxide: —

$$K_2CO_3 + Ca(OH)_2 = CaCO_3 + 2\,KOH.$$

The calcium carbonate being insoluble, is filtered off, while potassium hydroxide remains in solution.

It is readily obtained by treating a solution of potassium sulphate with a solution of the hydroxide of a metal whose sulphate is insoluble, such as barium hydroxide: —

$$K_2SO_4 + Ba(OH)_2 = BaSO_4 + 2\,KOH.$$

None of these methods are used extensively where it is desired to prepare potassium hydroxide upon the large scale. They have all been supplanted by the electrolytic method.

When a *concentrated aqueous solution of potassium chloride is electrolyzed,* the potassium ions move with the current to the cathode, but do not separate upon it. They find around the cathode a few hydrogen ions from the slightly dissociated water, and these, holding their charge less firmly than the potassium ions, give it up to the cathode and escape as hydrogen gas. The hydroxyl ions from the dissociated water, corresponding to the hydrogen ions which have escaped, remain in solution around the cathode, and with the potassium ions form potassium hydroxide.

The chlorine anions, having moved over to the anode, holding their charge less firmly than the hydroxyl ions from the dissociated water, give it up to the anode and escape as ordinary gaseous

chlorine. The reaction which takes place as the result of the decomposing action of the current may be represented thus: —

$$2\overset{+}{K}, 2\overset{-}{Cl} + 2\overset{+}{H}, 2\overset{-}{OH} = 2\overset{+}{K}, 2\overset{-}{OH} + H_2 + Cl_2.$$

If mercury is used as the cathode, the potassium dissolves in the mercury and forms potassium amalgam, which, when treated with water, forms potassium hydroxide and liberates hydrogen.

Potassium hydroxide dissolves very readily in water, forming *caustic potash*, and the solution is one of the strongest bases known. It dissociates completely into potassium and hydroxyl ions, —

$$KOH = \overset{+}{K}, \overset{-}{OH},$$

and this at no very great dilution. When a dilution of about 1000 litres is reached, the potassium hydroxide is completely dissociated into its ions. The great dissociation of this base is shown by the following very high conductivities, which are given for several dilutions: —

v	μ_v (18°)	a
1	171.8	80.3 per cent
10	198.6	92.8 per cent
100	212.0	99.1 per cent
μ_∞ 500	214.0	100.0 per cent

Potassium hydroxide, on account of its solubility, readily precipitates the hydroxides of the heavy metals from aqueous solutions of their salts: —

$$\overset{+}{Ag}, \overset{-}{NO_3} + \overset{+}{K}, \overset{-}{OH} = AgOH + \overset{+}{K}, \overset{-}{NO_3},$$

$$\overset{++}{Cd}, \overset{-}{Cl}, \overset{-}{Cl} + \overset{-}{OH}, \overset{+}{K} + \overset{-}{OH}, \overset{+}{K} = Cd(OH)_2 + \overset{+}{K}, \overset{-}{Cl} + \overset{+}{K}, \overset{-}{Cl},$$

$$\overset{+++}{Fe}, \overset{-}{Cl}, \overset{-}{Cl}, \overset{-}{Cl} + \overset{+}{Na}, \overset{-}{OH} + \overset{+}{Na}, \overset{-}{OH} + \overset{+}{Na}, \overset{-}{OH} =$$

$$Fe(OH)_3 + \overset{-}{Cl}, \overset{+}{Na} + \overset{-}{Cl}, \overset{+}{Na} + \overset{-}{Cl}, \overset{+}{Na}$$

Potassium hydroxide, on account of its strongly basic nature, acts vigorously upon organic matter, decomposing it into simpler substances. When brought in contact with the skin it disintegrates the organic matter and partly dissolves it.

The white, hard, solid potassium hydroxide melts at a red heat, and when in contact with the air at ordinary temperatures, absorbs carbon dioxide from it and forms the carbonate.[1] Potassium hydrox-

[1] Silver hydroxide, however, breaks down into silver oxide and water.

ide which has stood in contact with the air for any length of time, is, therefore, always contaminated with potassium carbonate. To free it from the carbonate it is dissolved in alcohol in which the carbonate is insoluble. When the alcoholic solution of the hydroxide is filtered to remove the carbonate, and evaporated away from all traces of carbon dioxide, the pure hydroxide is obtained and is known as *potassium hydroxide by alcohol.*

Compounds of Potassium with the Halogens. — Potassium combines with all of the four halogens, forming beautifully crystalline and stable compounds.

Potassium Chloride, KCl, occurs in nature in combination with magnesium chloride as the mineral *carnallite*, $KMgCl_3 . 6 H_2O$, and in other combinations. When a hot solution of this salt crystallizes, the double salt decomposes, potassium chloride separating out. Potassium chloride when it occurs in the pure condition is known as *sylvine.* It is a beautifully white substance, crystallizing in cubes, which are readily dissolved by water. It can be easily purified by crystallization, since it is far more soluble in hot water than in cold. At 0° one part of water dissolves 0.28 part of the salt, while at 100° one part of water dissolves 57 parts of the salt. Potassium chloride is a type of a salt of a strong acid with a strong base. We have seen that a strong acid and a strong base mean those which are greatly dissociated. The compound formed by the union of the cation of the base $\overset{+}{K}$, with the anion of the acid $\overset{-}{Cl}$, is among the most strongly dissociated substances known. At a dilution of 400 to 500 litres potassium chloride is completely dissociated into its ions $\overset{+}{K}$ and $\overset{-}{Cl}$. A dilute solution of potassium chloride is, therefore, a solution of potassium and chlorine ions and nothing else, there being no molecules in the solution. All the properties of such solutions, both chemical and physical, are the properties of chlorine ions and potassium ions, since these only are present. A study of the chemical and physical properties of such a solution proves this to be the fact. Such a solution shows in general the chemical reactions of potassium ions, and of chlorine ions, one of the most characteristic being the union with the silver ion forming silver chloride.

The physical properties of such solutions are always additive, as we say, *i.e.* the sum of two constants, one depending upon the cation, the other upon the anion. In this class belong the density, power to refract light, surface-tension, heat expansion, lowering of freezing-point, lowering of vapor-tension, and in general all physical properties.

Without the aid of the theory of electrolytic dissociation it has been impossible to interpret such facts; they can not only be interpreted by means of this theory, but are a necessary consequence of it.

Potassium chloride melts at 770° and passes into vapor at a white heat. When potassium chloride is fused with metallic potassium the *subchloride* K_2Cl is formed.

Potassium Bromide, KBr, is formed by the action of bromine on caustic potash: —

$$6\,KOH + 6\,Br = 5\,KBr + KBrO_3 + 3\,H_2O,$$

also by the action of caustic potash upon ferrous bromide: —

$$FeBr_2 + 2\,KOH = Fe(OH)_2 + 2\,KBr.$$

It is a beautifully crystalline solid, melting at 715°, and very soluble in water, one part dissolving in one part of water at 100°.

Its aqueous solution is completely dissociated at moderate dilution, yielding potassium and bromine ions. This salt furnishes us with one of the most convenient means of obtaining bromine ions in solution at any desired concentration.

Potassium Iodide, KI, is formed by treating ferrous iodide with caustic potash. The ferrous iodide is prepared by the action of iodine on iron in the presence of water. Ferrous iodide has the power to take up more iodine and form Fe_3I_8. When this compound is treated with potassium hydroxide or potassium carbonate, ferrous hydroxide is precipitated and potassium iodide remains in solution. It crystallizes from the solution on evaporation, in the form of beautifully white cubes. These melt at 625°, and are more soluble in water than even potassium bromide. One part of water at 0° dissolves 1.27 parts of potassium iodide.

The aqueous solution of potassium iodide, like the bromide and chloride, is completely dissociated at moderate dilution into potassium and iodine ions. By dissolving this compound in water we can easily prepare a concentrated solution of iodine ions.

Potassium Fluoride, KF, 2 H_2O, is formed by the action of hydrofluoric acid on potassium hydroxide. Like the remaining halogen compounds of potassium it is a white solid; unlike them, however, it crystallizes with two molecules of water. When potassium fluoride is treated with an equivalent of hydrofluoric acid it forms the compound KHF_2, which, together with other facts, points to the dibasic nature of hydrofluoric acid.

Hydrofluoric acid, then, probably has the composition H_2F_2, potassium fluoride the composition K_2F_2, and the acid salt, KHF_2.

Potassium Chlorate, $KClO_3$. — Potassium combines with the oxygen acids of chlorine, forming well-defined salts. A few of these are of sufficient importance to merit special consideration. Potassium chlorate is prepared, as we have seen, by the action of chlorine on caustic potash: —

$$6\,KOH + 3\,Cl_2 = 5\,KCl + KClO_3 + 3\,H_2O.$$

It is separated from the chloride by its solubility in water being much less than that of the chloride. It is also formed by the action of potassium chloride on calcium chlorate. When chlorine obtained electrolytically is conducted into lime calcium hypochlorite is formed. When a solution of calcium hypochlorite is boiled it passes into the chlorate and chloride: —

$$3\,Ca(OCl)_2 = Ca(ClO_3)_2 + 2\,CaCl_2.$$

When the solution of calcium chlorate is treated with a solution of potassium chloride the following reaction takes place: —

$$Ca(ClO_3)_2 + 2\,KCl = CaCl_2 + 2\,KClO_3.$$

Potassium chlorate, on account of its smaller solubility, is formed and can be readily obtained from the solution in beautiful white plates.

When potassium chlorate is heated it decomposes in the sense of the following equation: —

$$2\,KClO_3 = KCl + KClO_4 + O_2,$$

potassium chloride and perchlorate being formed. When the perchlorate is heated to a still higher temperature it breaks down into the chloride and oxygen. Potassium chlorate is useful chiefly because of the large amount of oxygen which it contains and which it can readily give up. It is, therefore, an excellent oxidizing agent, and as such is useful in chemistry. Its oxidizing power is due to the ease with which the chloric ion $\overline{ClO_3}$ passes into the chlorine ion $\overline{Cl}$, liberating three oxygen atoms. This decomposition takes place with the evolution of a large amount of heat, which explains the violent nature of such reactions as the following: —

When potassium chlorate is powdered with a small piece of sulphur, an explosion occurs, which is violent if an appreciable quantity of sulphur is used. A violent explosion results if potassium chlorate is brought together with phosphorus. With antimony sulphide an explosive mixture is also formed.

Potassium chlorate is extensively used in the preparation of matches. The so-called *safety matches* are made of a mixture of

potassium chlorate and sulphide of antimony. When these are rubbed upon a surface covered with red phosphorus, a miniature explosion results and the whole mass is ignited. When rubbed upon an ordinary object such matches do not take fire.

When treated with concentrated sulphuric acid potassium chlorate liberates oxides of chlorine, which are unstable and frequently explode with great violence. The instability of these compounds accounts for the reaction when a mixture of sugar and potassium chlorate is treated with sulphuric acid. They break down, and in doing so liberate enough heat to ignite the cane-sugar.

Potassium Perchlorate, $KClO_4$, is prepared, as we have already seen, by heating potassium chlorate carefully until the molten mass has resolidified and the first evolution of oxygen has practically ceased. The salt is of interest because it contains more oxygen than potassium chlorate, and is still a much more stable compound, giving up its oxygen only at a considerably higher temperature. This undoubtedly has to do in some way with the manner in which the oxygen is combined in the compound — with the constitution of the compound. It cannot be explained if we regard the molecule as simply a material system, and disregard the way in which the system is made up. It may have to do also with the arrangement of the atoms in space — with the stereochemistry of the molecule. By adding one oxygen atom to potassium chlorate the geometrical configuration of the molecule may be so changed as to form a more stable system. In reference to these matters we at present, however, know nothing, and but little is gained by speculation. Potassium perchlorate is of importance on account of its small solubility in water, one gram of the salt dissolving in 143 grams of water at 0°. If alcohol is added to the water the solubility of potassium perchlorate is still further greatly diminished. This is one of the few difficultly soluble salts which potassium forms with acids, and is, therefore, used to *detect the presence of potassium in a solution of potassium ions.*

Potassium Hydrazoate, KN_3, and Potassium Amide, KNH_2. — The potassium salt of hydrazoic or triazoic acid is formed when a solution of potassium hydroxide is neutralized with hydrazoic acid. It resembles in its appearance potassium chloride, and in its properties the sodium salt of this acid.

Potassium amide is formed by conducting carefully dried ammonia over metallic potassium. One hydrogen atom of the ammonia is set free and potassium takes its place: —

$$2\,NH_3 + 2\,K = 2\,KNH_2 + H_2.$$

When potassium amide is treated with nitrous oxide, potassium hydrazoate is formed: —

$$2\,KNH_2 + N_2O = KOH + NH_3 + KN_3.$$

This reaction is strictly analogous to that which we have already studied under the element sodium.

Potassium Nitrate, KNO_3. — Potassium nitrate or saltpetre is one of the most important salts of potassium. It is very soluble in water and, therefore, does not occur in the solid state in any considerable quantity in regions where there is an abundant rainfall. It is, however, leached out of the soil in certain regions in the East Indies during the rainy season, and deposited when the rain has ceased. This is known as the "India crude saltpetre."

Potassium nitrate is formed in large quantity in the *saltpetre plantations*. Refuse animal matter which contains nitrogen is mixed with potassium or calcium carbonate, or with earth or wood-ashes containing these substances, and exposed to the action of the "nitrifying ferment" or "saltpetre bacteria" in the soil. The oxygen of the air, through the agency of these bacteria, oxidizes the ammonia formed from the decomposing organic matter, to nitric acid, which then combines with potassium or calcium hydroxide or carbonate and forms the corresponding nitrate. After the action has continued for several years the whole mass is treated with water, which dissolves all of the nitrates, including in addition to potassium especially those of calcium and magnesium. The mixture of nitrates is treated with the product of the leaching of wood-ashes, *i.e.* with a solution of potassium carbonate. Calcium and magnesium carbonates are precipitated, and potassium nitrate remains behind in solution.

Frequently, nitrates are formed around stables and other places where organic matter is undergoing decomposition, and in rainless regions this forms incrustations which are dissolved in water and converted into saltpetre.

Potassium nitrate is made to-day chiefly from sodium nitrate or Chili saltpetre. When a solution of sodium nitrate is mixed with a solution of potassium chloride, the following reaction takes place: —

$$\overset{+}{Na},\ \overset{-}{NO_3} + \overset{+}{K},\ \overset{-}{Cl} = NaCl + \overset{+}{K},\ \overset{-}{NO_3}.$$

The sodium chloride is deposited at higher temperatures. When the solution is allowed to cool down, potassium nitrate is deposited. The reason why this reaction takes place is found in the relative solubilities of the four salts, potassium and sodium chlorides and potassium and sodium nitrates.

These relations are shown in Fig. 35. At the higher temperatures the solubility of sodium chloride is less than that of potassium chloride, and much less than that of potassium nitrate. It, therefore, separates when the solution is concentrated at the higher temperature. Further, the solubility of sodium chloride is as great at 0° as at 100°. When a solution saturated with sodium chloride at 100° is allowed to cool down to 0°, it will, therefore, be only saturated at the lower temperature and will not deposit any of the salt. On the other hand, potassium nitrate is many times as soluble at 100° as

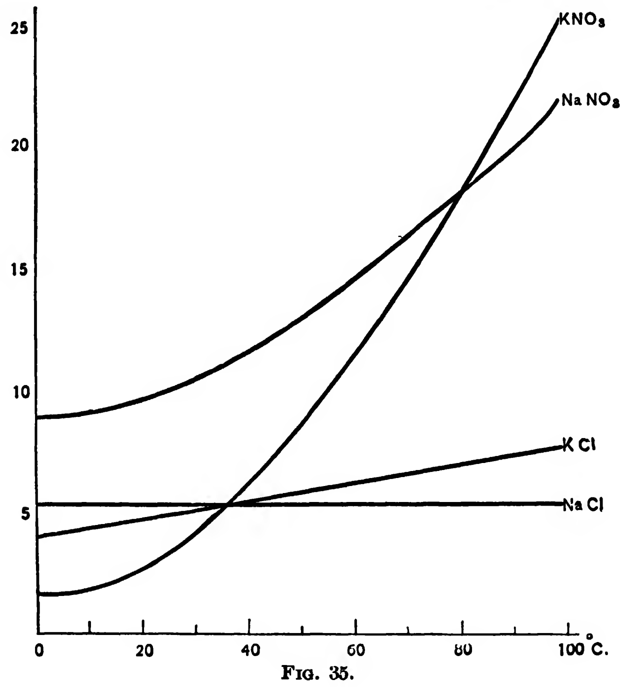


FIG. 35.

at 0°. When a solution of potassium nitrate which is far from saturated at 100° is cooled down it will, therefore, deposit crystals long before zero degrees is reached.

These solubility curves explain more at a glance concerning the reason why the above transformation takes place, than could be done by pages of description. When the solution is evaporated sodium chloride separates from it while hot. This is removed and the solution allowed to cool, when potassium nitrate crystallizes out. This process is repeated a few times when the transformation indicated by the above equation is practically complete.

Potassium nitrate readily gives up a part of its oxygen and is, therefore, an excellent oxidizing agent. It is, therefore, used where rapid oxidization is desired, such as in fireworks and especially in gunpowder. *Gunpowder* is a mixture of potassium nitrate, sulphur, and carbon, in such proportions as to secure complete combustion. The nitrate gives off oxygen, which combines with the carbon forming carbon dioxide; the nitrogen escapes as such, and the potassium remains behind in the form of sulphide or sulphate. The equation which is usually written to express the decomposition of gunpowder is:—

$$2\,KNO_3 + 3\,C + S = K_2S + 3\,CO_2 + N_2.$$

This is an idealized equation, the reaction which takes place being far more complex than it would indicate. In addition to the above products, when gunpowder decomposes there are formed potassium sulphate, potassium sulphide, potassium carbonate, and carbon monoxide.

Gunpowder is prepared by mixing the three constituents in the following proportions:—

KNO_3	75 per cent
S	12 per cent
C	13 per cent

This corresponds almost exactly to three molecules of saltpetre, three atoms of carbon, and one atom of sulphur, and is the chief reason for writing the above very simple equation.

The reactions which take place are, as already stated, far more complicated.

When gunpowder is ignited, the gases liberated occupy several hundred times the volume of the powder; or if they are forced to occupy the same volume as the original powder, the pressure exerted is several hundred atmospheres. This is the principle made use of in employing explosives to drive missiles with a high velocity. The gunpowder is exploded in a metal tube closed on all sides and open at one end. The ball is placed tightly upon the powder, so that when the latter explodes the gases are liberated in practically a closed space. An enormous pressure is thus generated, which drives the ball out of the end of the gun with a high velocity. In calculating the force produced by an explosion of gunpowder, we should always take into account the further fact that the gases are greatly heated by the heat energy produced as the result of the reaction, and, therefore, in approximate accordance with the law of Gay-Lussac, exert a still greater pressure.

Potassium Nitrite, $KNO_2 . H_2O$.—When potassium nitrate is carefully heated it melts at about 338°. When heated higher it loses oxygen and forms potassium nitrite:—

$$2\,KNO_3 = 2\,KNO_2 + O_2.$$

This is the method by which oxygen was first prepared by its discoverer, the great Swede, Scheele. Potassium nitrite is best prepared by heating the nitrate with a mild reducing agent, such as metallic lead:—

$$KNO_3 + Pb = KNO_2 + PbO.$$

Under these conditions there is less decomposition of the compounds, and, altogether, the reaction is a much smoother one. It is also formed by neutralizing a solution of nitrous acid with potassium hydroxide. When potassium nitrite is treated with a strong acid nitrous acid is liberated. It can, therefore, be used as a means of preparing nitrous acid. The potassium salt of nitrous acid, like the salts of weak acids in general, is hydrolyzed to some extent by water:—

$$\overset{+}{K},\ \overset{-}{NO_2} + H_2O = \overset{+}{K},\ \overset{-}{OH} + HNO_2.$$

Nitrous acid, HNO_2, being a weak acid, is only slightly dissociated, and, therefore, there are many more hydroxyl ions in the above solution than hydrogen ions, and the solution reacts alkaline.

Compounds of Potassium with Sulphur.—The compounds of potassium with sulphur do not present many points of difference from those of sodium. *Potassium hydrosulphide*, KSH, $\frac{1}{2}H_2O$, is formed when hydrogen sulphide is conducted into a solution of potassium hydroxide:—

$$KOH + H_2S = H_2O + KSH.$$

This being a salt of a weak acid, is hydrolyzed by water, showing an alkaline reaction:—

$$\overset{+}{K},\ \overset{-}{SH} + H_2O = \overset{+}{K},\ \overset{-}{OH} + \overset{+}{H},\ \overset{-}{HS}.$$

Since hydrogen sulphide is a weak acid, there are only a few hydrogen ions in the solution, and the hydroxyl ions show basic or alkaline reactions.

When an equivalent of potassium hydroxide is added to potassium hydrosulphide, the *normal sulphide* $K_2S . 5H_2O$ is formed:—

$$KSH + KOH = K_2S + H_2O.$$

This is also strongly hydrolyzed by water:—

$$K_2S + H_2O = \overset{+}{K},\ \overset{-}{OH} + \overset{-}{HS},\ \overset{+}{K}.$$

When sulphur is added to a hot solution of potassium sulphide, it dissolves and forms *polysulphides* varying in composition from K_2S_3 to K_2S_5

Compounds of Potassium with Sulphur and Oxygen. — When sulphur dioxide is passed into a solution of potassium hydroxide or carbonate, *potassium sulphite*, K_2SO_3, is formed. If the gas is passed through the solution until the solution will take up no more of it, the *acid sulphite* $KHSO_3$ results.

The potassium salt of *persulphuric acid*, KSO_4 or $K_2S_2O_8$, is a well-crystallized substance. It is obtained by electrolyzing acid potassium sulphate, and separates from the solution on account of it being difficultly soluble.

Potassium Sulphate, K_2SO_4, occurs in nature in combination with magnesium sulphate and magnesium chloride as *kainite*. This occurs in a number of the salt-beds, but especially in those at Stassfurt and other places in Germany. Kainite has the composition $K_2SO_4 \cdot MgSO_4 \cdot MgCl_2 \cdot 6H_2O$. The double sulphate of potassium and magnesium is treated with chloride of potassium, when magnesium chloride and potassium sulphate result. This salt is used to prepare potassium carbonate. It is also used in the preparation of the double sulphate of potassium and aluminium, or ordinary potassium alum. It is extensively used as kainite to enrich the soil in potassium ions, which are so much needed by many plants. Potassium sulphate is not very soluble in water, one part of water at 0° dissolving only 0.085 part of the salt.

When normal potassium sulphate is treated with an equivalent of sulphuric acid the *acid, or primary sulphate*, is formed: —

$$K_2SO_4 + H_2SO_4 = 2KHSO_4.$$

While the normal sulphate of potassium is only slightly soluble in water, the acid sulphate is very soluble, one part of water dissolving 0.33 parts of the salt at 0°. Acid potassium sulphate occurs in nature in certain volcanic regions, as in those of Naples, as the mineral *misenite*.

When acid potassium sulphate is heated it melts at 200°. When heated in a vacuum to 300° it passes over into the *pyrosulphate*: —

$$2KHSO_4 = H_2O + K_2S_2O_7.$$

When heated still higher it decomposes, giving water and sulphur trioxide: —

$$2KHSO_4 = H_2O + K_2SO_4 + SO_3,$$

or,

$$K_2S_2O_7 = K_2SO_4 + SO_3.$$

The sulphur trioxide thus set free dissolves oxides of metals converting them into sulphates, decomposes insoluble silicates forming soluble compounds, and in general is a powerful reagent. When it is desired to remove insoluble substances adhering to platinum vessels, the best method is to partly fill the vessel with acid potassium sulphate, and heat the mass until there is a copious evolution of sulphur trioxide.

Acid potassium sulphate in aqueous solution shows a strongly acid reaction. This is due to the fact that sulphuric acid is a strong acid and the second hydrogen ion begins to dissociate.

$$KHSO_4 = \overset{+}{K}, \overset{+}{H}, \overset{=}{SO_4}.$$

Acid potassium sulphate is of interest in connection with the development of the conception of mass action. Heinrich Rose, who pointed out the action of carbon dioxide on silicates over the surface of the earth, also called attention to the following facts. When a boiling solution of acid potassium sulphate of medium concentration is crystallized, the crystals have the composition expressed by the formula $3\,K_2SO_4 . H_2SO_4$, a portion of the sulphuric acid having been split off to combine with the water. If these crystals are redissolved in more water, and the solution evaporated to crystallization, the neutral salt will separate, showing a further splitting off of sulphuric acid due to the mass action of the water.

We can now understand how this reaction takes place. In an aqueous solution of acid potassium sulphate there are both potassium ions and sulphuric ions $\overset{=}{SO_4}$. When the conditions of concentration are properly established, these ions combine directly and form the neutral sulphate.

Potassium Carbide, K_2C_2. — Metallic potassium acts directly upon acetylene, forming the carbide of potassium: —

$$C_2H_2 + 2\,K = C_2K_2 + H_2.$$

In the presence of water this breaks down, yielding potassium hydroxide and acetylene.

Potassium Carbonate, K_2CO_3. — Potassium carbonate was obtained for a long time mainly from the ashes of certain plants. When the plants were burned the potassium remained behind in the form of the carbonate. This was obtained by leaching the ashes with water and evaporating the solution, when the impure carbonate crystallized out. The impurities are in the main potassium sulphate and chloride and salts of sodium, all of which are less soluble than potassium carbonate. The carbonate is purified by means of the

difference in solubility between the impurities and the salt in question. It dissolves, and for the most part leaves the impurities behind. This impure mass is known as *potash*, the purified carbonate as *purified potash.*

Potassium carbonate is also obtained from the residues of the beet-sugar industry.

Potassium carbonate can also be prepared by the action of magnesium carbonate and carbon dioxide under pressure on potassium chloride. There is formed the double carbonate of potassium and magnesium, $KHCO_3$, $MgCO_3 . 4\,H_2O$, which, when decomposed with water at a high temperature, yields potassium carbonate in solution.

Potassium carbonate is also prepared by the electrolysis of potassium chloride. Around the cathode in a concentrated solution of potassium chloride, potassium hydroxide is formed. Carbon dioxide is conducted into this solution, and potassium carbonate is formed. Potassium carbonate is remarkably soluble in water, one part of water at 0° dissolving 0.83 parts of the salt, and the solubility increases rapidly with rise in temperature.

Potassium carbonate takes up water from the air, or is deliquescent. From the cold, aqueous solution a salt separates, containing three molecules of water to two of potassium carbonate, $2\,K_2CO_3 . 3\,H_2O$. Potassium carbonate melts a little above 1000°.

The aqueous solution of potassium carbonate shows a strong alkaline reaction. This is due to the hydrolysis of the salt of the weak carbonic acid: —

$$\overset{+}{K}, \overset{+}{K}, \overset{=}{CO_3} + H_2O = \overset{+}{K}, \overset{-}{OH} + H\overset{-}{CO_3}, \overset{+}{K},$$

which takes place to a very considerable extent, yielding a large number of hydroxyl ions, which react strongly alkaline.

Acid, or Primary Potassium Carbonate, $KHCO_3$. — The acid salt is formed by conducting carbon dioxide into the solution of the neutral salt: —

$$K_2CO_3 + CO_2 + H_2O = 2\,KHCO_3,$$

or, if we express this in terms of the ions: —

$$\overset{+}{K}, \overset{+}{K}, \overset{=}{CO_3} + CO_2 + H_2O = \overset{+}{K}, H\overset{-}{CO_3} + H\overset{-}{CO_3}, \overset{+}{K}.$$

Dilute solutions of acid potassium carbonate react alkaline. At first sight it may seem peculiar that an acid salt should show an alkaline reaction, when there is still one acid hydrogen present in the molecule. This was entirely unexplained until the theory of electrolytic dissociation arose. Now we know that it is simply due to the hydrolysis of the acid salt by water, forming hydroxyl ions: —

$$KHCO_3 + H_2O = \overset{+}{K}, \overset{-}{OH} + H_2CO_3.$$

When acid potassium carbonate is heated it decomposes, forming the normal carbonate, carbon dioxide, and water: —

$$2\,KHCO_3 = K_2CO_3 + H_2O + CO_2.$$

If an aqueous solution is boiled the same decomposition takes place. This continues in either case until the carbon dioxide has reached a certain pressure or density, or better expressed, concentration, which is proportional to pressure.

When, at any given temperature the pressure of the carbon dioxide has reached a certain value, equilibrium is established, and as much carbon dioxide is absorbed in any given time as is set free. If the pressure of the carbon dioxide is increased at this temperature, the following reaction takes place: —

$$K_2CO_3 + CO_2 + H_2O = 2\,KHCO_3.$$

This will be recognized to be exactly the reverse of the above decomposition, so that we have here an excellent example of a reversible reaction. If, when equilibrium is established, pressure of the carbon dioxide is diminished, more of the acid carbonate will decompose, until the equilibrium pressure is again established.

If when equilibrium is established at any one temperature, the temperature is not kept constant but varied, the equilibrium will be destroyed; and more of the acid carbonate will decompose, or will be formed, until the pressure of the gas is such as to establish equilibrium at the new temperature. When the carbon dioxide is allowed to escape as fast as it is formed, its pressure is practically zero, and nearly all of the acid carbonate can be transformed into neutral carbonate under these conditions.

Phosphates of Potassium. — Potassium combines with phosphorus when the two elements are heated together, and forms the compound KP_5 — *potassium phosphorus.*

Potassium, like sodium, forms three salts with phosphoric acid, — the primary, KH_2PO_4; secondary, K_2HPO_4; and tertiary, K_3PO_4, phosphates.

These phosphates do not call for any special comment. They are all readily soluble in water, yielding potassium ions and phosphoric acid ions, both of which are needed for the growth and seeding of plants. They are, therefore, among the most valuable compounds known as artificial fertilizers. When these compounds are heated, they undergo decompositions which are similar to those suffered by

the corresponding sodium compounds; the secondary phosphate yielding a pyrophosphate: —

$$2\,K_2HPO_4 = H_2O + K_4P_2O_7.$$

The primary phosphate gives off water and forms the metaphosphate: —

$$KH_2PO_4 = H_2O + KPO_3.$$

Silicates of Potassium. — Finely powdered sand, fused with potassium hydroxide, or potassium carbonate, becomes soluble in water. The thick, syrupy mass is supposed to be made up of a number of compounds from which no one substance has thus far been isolated. The syrup dissolves readily in water, and when the aqueous solution is allowed to dry a vitreous mass is left behind. It is, therefore, known as potassium water-glass. When inflammable objects are covered with water-glass they become more or less fire-proof, since the covering prevents access of oxygen to them unless they are subjected to high temperatures. When a solution of the silicates of potassium is treated with an acid, a heavy, white precipitate of silicic acid is thrown down.

Potassium Silicofluoride, K_2SiF_6. — This salt is formed when hydrofluosilicic acid is added to a solution of a potassium salt: —

$$K_2SO_4 + H_2SiF_6 = H_2SO_4 + K_2SiF_6.$$

This salt is comparatively insoluble in water and is, therefore, useful in detecting the presence of potassium. The index of refraction of the salt is almost exactly the same as that of water, and it is, therefore, very difficult to see when suspended in water. Unless precaution is taken to examine in different lights the liquid in which the precipitate may be suspended, its presence can be easily overlooked.

When potassium silicofluoride is treated with a strong alkali the compound is decomposed into the alkaline fluoride and silicic acid: —

$$K_2SiF_6 + 4\,NaOH = 2\,KF + 4\,NaF + Si(OH)_4.$$

Potassium Pyroantimoniate, $K_4Sb_2O_7$, is formed by fusing antimonic acid with an excess of potassium hydroxide. When treated with water it breaks down into potassium hydroxide and the salt $K_2H_2Sb_2O_7$. Although this salt is not very soluble in water, it is far more soluble than the corresponding sodium salt. When a solution of the potassium salt is added to a solution of a sodium salt, the insoluble sodium pyroantimoniate, as we have seen, is thrown down.

Potassium Cyanide, KCN. — Potassium cyanide is formed when organic substances containing nitrogen and carbon are heated with metallic potassium. This reaction with potassium or sodium is frequently made use of to detect the presence of nitrogen in organic compounds. It is formed on the large scale by passing ammonia over a mixture of carbon and potassium carbonate. It is also formed in the blast-furnace where carbon and nitrogen are brought together at very high temperatures. It is obtained in pure condition from a salt which we shall study when we come to iron — potassium ferrocyanide, $K_4Fe(CN)_6$. When heated alone it gives potassium cyanide — one-third of the cyanogen being lost. By heating this with metallic potassium iron is thrown out and potassium cyanide remains: —

$$K_4Fe(CN)_6 + 2\,K = 6\,KCN + Fe.$$

Potassium cyanide is readily soluble in water. Being a salt of a weak acid it is hydrolyzed by water, and its aqueous solution always smells of hydrocyanic acid: —

$$KCN + H_2O = \overset{+}{K},\ \overset{-}{O}H + HCN.$$

Hydrocyanic acid is very slightly dissociated by water, existing in solution mainly as molecules. The solution has a certain vapor-tension of hydrocyanic acid, and this is sufficient to produce a detectable odor.

Potassium cyanide is a very powerful poison. It is a good reducing agent at an elevated temperature, taking up oxygen and passing over into the *cyanate, KOCN;* or sulphur, and passing over into the *sulphocyanate, KSCN.* When potassium sulphocyanate is dissolved in water a large amount of heat is absorbed, and a marked refrigerating effect is produced. Potassium cyanide is extensively used in connection with the extraction of gold from ores which are not very rich, and in connection with the electrolytic deposition of many of the metals.

Oxalates of Potassium. — Potassium forms three well-defined and stable compounds with oxalic acid. These are the best-known salts of oxalic acid, since they occur in abundance in certain plants. The *normal oxalate,* $K_2C_2O_4 . H_2O$, can be easily prepared by neutralizing oxalic acid completely with caustic potash. The *acid oxalate,* $KHC_2O_4 . \frac{1}{2}\,H_2O$, is prepared by treating the neutral salt with one equivalent of oxalic acid. Like the neutral salt it occurs abundantly in certain plants as the wood-sorrel, from which it can be readily extracted.

Potassium forms still another oxalate with oxalic acid, which is

more acid than the acid oxalate. This is the *tetroxalate of potassium*, $KHC_2O_4 . H_2C_2O_4 . 2 H_2O$. In this compound there is one equivalent of potassium to two molecules of oxalic acid, or the oxalic acid is just one-fourth neutralized by potassium. It is readily prepared by bringing either of the above oxalates together with the necessary amount of oxalic acid, and allowing the salt to crystallize from the hot, concentrated solution. Although the molecule is fairly complex it is perfectly stable in the air, and is very useful in analytical chemistry, since the salt can be weighed. It is now used in many analytical operations where oxalic acid was formerly employed, since oxalic acid gives off water when exposed to the air, and we are never quite certain whether it possesses just two molecules of water of crystallization. When a standard solution is desired containing just so much oxalic acid, the corresponding amount of tetroxalate is employed.

The tetroxalate is now extensively used in standardizing solutions of potassium permanganate, and in many similar operations where oxalic acid was formerly employed, for the reason indicated above.

Detection of Potassium. — Potassium is most readily detected by means of the flame reaction. When a potassium salt or a substance containing potassium is introduced into the flame, the latter gives out a reddish-violet light which is very characteristic. If the potassium salt contains a sodium salt mixed with it, the intense yellow of the sodium flame may entirely mask the far less intense color of the potassium flame. In such cases it is necessary to cut out the sodium light in order to see whether there is any of the potassium flame present. This is accomplished by allowing the light to pass through blue, cobalt glass, which cuts off all of the yellow, but allows the short wave-lengths sent out by the potassium to pass through. When the flame emitted by both sodium and potassium is examined through cobalt glass, the sodium yellow is not seen at all, and the potassium flame appears redder than when alone and examined with the naked eye. The flame test, correctly made, is a very sensitive means of detecting the presence of small quantities of potassium.

We have now studied sodium and potassium with some thoroughness. The remaining alkali metals, lithium, cæsium and rubidium, are comparatively rare substances and will be treated briefly.

CHAPTER XXIX

LITHIUM, RUBIDIUM, CÆSIUM, (AMMONIUM)

LITHIUM (At. Wt. = 7.03)

Discovery, Preparation, and Properties. — Lithium was discovered as early as 1817, but was not isolated until 1855, when Bunsen obtained it by electrolyzing the chloride. Lithium is widely distributed in nature but occurs only in relatively small quantities. Lithium occurs as the silicate in the minerals *lepidolite spodumene, tourmaline*, etc., as the phosphate combined with other phosphates in *amblygonite* and *triphylite.* As already stated Bunsen electrolyzed the chloride. The best results are obtained by dissolving the anhydrous chloride in some solvent which does not act chemically upon the metal. Pyridine is such a solvent. A pyridine solution of the chloride conducts the current very readily, and from this solution lithium readily separates upon the cathode.

Lithium resembles sodium very closely in its properties. It is of nearly the same color, but is much harder than sodium and can be drawn into wire. It quickly tarnishes in contact with the air, due to the combination with oxygen. It acts upon water, forming the hydroxide and liberating hydrogen, which, however, is not ignited, and the metal is not melted by the heat set free. Lithium is the lightest of all known metals, having a specific gravity of 0.59. It melts at 186°, and does not take fire in the air until about 200° is reached.

Lithium forms the univalent cation $\overset{+}{Li}$, which acts like the univalent sodium and potassium cations, combining with the anions of acids, forming salts. A few of these substances will be considered.

Compounds of Lithium. — The compounds of lithium closely resemble those of sodium and the other alkalies. In a few cases, however, differences appear which are worthy of note. Unlike the remaining alkalies lithium forms an *oxide*, Li_2O, which dissolves only slowly in water forming the *hydroxide*, LiOH. The hydroxide is dissociated by water in the same manner as the hydroxides of the remaining alkalies: —

$$LiOH = \overset{+}{Li}, \overset{-}{OH}.$$

There is a large number of hydroxyl ions present and the solution, therefore, reacts strongly alkaline.

Lithium forms the *hydride* LiH, which reacts with water as follows: —

$$LiH + H_2O = H_2 + LiOH.$$

The *lithium halides* resemble those of sodium, being, however, deliquescent or absorbing moisture from the air. They differ from the halides of the other alkalies in being soluble in a mixture of alcohol and ether. Lithium forms with chlorine a *subchloride*, Li_2Cl. The *fluoride* of lithium is practically insoluble in water, and thus resembles more closely the fluoride of calcium than that of sodium and the remaining alkalies.

The *carbonate of lithium*, Li_2CO_3, presents certain points of interest. Unlike the carbonates of the alkalies it is difficultly soluble in water, one part of the salt requiring about one hundred parts of water to dissolve it. In this respect it resembles the carbonates of the alkaline earths. The *bicarbonate*, $LiHCO_3$, is much more soluble than the carbonate, and in this, again, lithium resembles the alkaline earths, as we shall see.

The *tertiary or normal lithium phosphate*, $Li_3PO_4 . \frac{1}{2}H_2O$, presents the same difference from the phosphates of the alkalies. It is nearly insoluble in water; one part of the phosphate requiring more than 2500 parts of water to dissolve it; and if ammonia is present, one part of the phosphate requires about 4000 parts of ammonia water to dissolve it. This salt furnishes us with a means of detecting the presence of a small amount of lithium. When a solution of a soluble phosphate, such as disodium phosphate, is treated with a solution of a lithium salt, lithium phosphate is precipitated: —

$$Na_2HPO_4 + 3\,LiCl = 2\,NaCl + HCl + Li_3PO_4.$$

The precipitation takes place in the presence of the hydrochloric acid, which is set free. Here again lithium resembles the alkaline earth metals, which form phosphates that are insoluble in water.

Lithium urate is soluble in water, and it has been supposed that by drinking water containing considerable lithium, the uric acid deposited in joints, muscles, etc., could be transformed into the soluble lithium salt and removed from the body in solution. How much truth there is in this assumption it is impossible at present to say.

Lithium gives two characteristic lines in the spectroscope, one in the yellow and the other in the red. It imparts a distinctly red color to the flame.

RUBIDIUM (At. Wt. = 85.5)

Occurrence, Preparation, Properties. — Rubidium occurs widely distributed in nature, but nowhere in large quantities. It occurs in *carnallite, lepidolite, leucite,* etc., and with potassium salts at Stassfurt. It is also present in small quantities in the waters of certain salt-wells, and was first discovered here by Bunsen and Kirchhoff in 1860. As the result of the application of the spectroscope, with which they had accomplished so much, they found in the liquor from the Dürkheim salt-wells lines which they could not identify as belonging to any known substance. They succeeded in isolating two substances, one of which gave two lines in the dark red, and was, therefore, called rubidium.

Rubidium is prepared by heating the hydroxide with magnesium: —

$$2\,RbOH + 2\,Mg = 2\,MgO + H_2 + 2\,Rb.$$

Rubidium resembles potassium in appearance and properties. It decomposes water with even greater violence than potassium, forming the hydroxide. It is soft at ordinary temperature, melting at 158°.

Compounds of Rubidium. — Rubidium unites with dry oxygen at ordinary temperatures, forming the *dioxide,* RbO_2. It forms dark-brown plates, melting at about 500°. When treated with water rubidium dioxide forms *rubidium hydroxide* and liberates oxygen. The hydroxide is also formed by treating rubidium carbonate with calcium hydroxide, or rubidium sulphate with barium hydroxide. It is a slightly stronger base than potassium hydroxide, dissociating to a slightly greater extent at the same dilution.

The *halides* of rubidium resemble in general those of potassium, but are more soluble. In addition to the ordinary chloride, bromide, and iodide, rubidium forms compounds containing two halides, such as $RbICl_4$, and $RbIBr_2$. These are formed by bringing chlorine and bromine, respectively, in contact with rubidium iodide. In such compounds rubidium seems to have a valence much greater than unity.

Notwithstanding the greater solubility of rubidium salts in general, the *perchlorate,* $RbClO_4$, is far less soluble than potassium perchlorate.

The *sulphate,* Rb_2SO_4, and *acid sulphate,* $RbHSO_4$, of rubidium resemble the corresponding potassium salts. When the acid sulphate is heated it readily yields the *pyrosulphate:* —

$$2\,RbHSO_4 = H_2O + Rb_2S_2O_7,$$

but this is far more stable than the corresponding potassium compound.

Rubidium forms insoluble compounds with hydrofluosilicic acid, hydrochlorplatinic acid, etc.; and it is, therefore, very difficult to separate rubidium from potassium. The salt with hydrochlorplatinic acid is, however, still less soluble than the corresponding potassium salt, and this difference has been utilized to effect a partial separation.

CÆSIUM (At. Wt. = 132.9)

Occurrence, Compounds. — Cæsium was first discovered by Bunsen in 1860, in the waters of the Durkheim salt-wells. In addition to the two dark lines which led to the discovery of rubidium, he obtained, after boiling down an enormous volume of the mineral water, a few grams of the chloride of a substance which, when examined spectroscopically, showed two lines in the blue. From the blue color of its spectrum lines he termed this element cæsium. It was first isolated in 1881 by the electrolysis of the fused cyanide. Cæsium also occurs as the silicate in the mineral *pollux* from the isle of Elba. The metal melts at 26°.5.

The compounds of cæsium resemble closely those of potassium and rubidium. They are in general a little more soluble than the corresponding compounds of rubidium. The *hydroxide* is even a little stronger base than rubidium hydroxide. Cæsium is, therefore, the strongest base-forming, or most electropositive, of all the elements. Like rubidium, it apparently shows a valence greater than unity towards certain of the halogens, especially iodine. It forms with iodine the pentaiodide CsI_5. Certain of the double compounds of cæsium are less soluble than the corresponding compounds of rubidium, and these are used in separating the two elements.

AMMONIUM

The group ammonium, although not an element, closely resembles in its properties the alkali metals. It forms a univalent cation, $\overset{+}{N}H_4$, which has the power to combine with the anions of acids and form salts, which resemble in many respects those of the alkali metals. As has already been mentioned, it combines with mercury like the alkalies and forms an amalgam, which, however, is very unstable.

Ammonium Hydroxide, NH_4OH. — Ammonia combines with water, forming the hydroxide NH_4OH: —

$$NH_3 + H_2O = NH_4OH.$$

In the presence of water this compound is dissociated to some extent into the ammonium ion, $\overset{+}{N}H_4$, and the hydroxyl ion, $\overset{-}{O}H$: —

$$NH_4OH = \overset{+}{N}H_4, \overset{-}{O}H.$$

It is, therefore, a base, but it is a very weak base. The small amount of its dissociation is shown by its small conductivity.

v	μ_v
10	3.1
100	9.2
1000	26.0
10000	61.0
50000	70.0

The concentration of hydroxyl ions in a normal solution of ammonia as compared with a normal solution of sodium hydroxide is about as 1 to 100. Ammonium hydroxide is, therefore, a relatively weak base.

Before we had the conductivity method of measuring the dissociation of bases and, therefore, their relative strengths, ammonium hydroxide was regarded as a strong base, probably in part on account of its action on the olfactory nerves and mucous membrane. This error has been once for all corrected by the conductivity method.

When an aqueous solution of ammonium hydroxide is boiled it breaks down into ammonia and water: —

$$NH_4OH = NH_3 + H_2O.$$

This fact is made use of in detecting the presence of ammonia or an ammonium salt. The ammonium salt is treated with a strong base like caustic soda, when it is broken down into the sodium salt, and ammonia which is given off when the solution is heated. This can be detected by the odor when present in considerable quantity, or by holding a piece of moistened red litmus in the escaping vapors, when the ammonia is present in small quantity. This becomes colored blue.

Although a solution of ammonium hydroxide is only slightly dissociated, it forms salts with practically all acids. Some of these have characteristics which are sufficiently interesting to merit special consideration.

Ammonium Chloride, NH_4Cl. — When hydrochloric acid is neutralized with ammonium hydroxide and the solution evaporated, am-

monium chloride or *sal ammoniac* is obtained. This salt is a beautifully crystalline compound, which is readily soluble in water. Although ammonium hydroxide is only slightly dissociated, the salt with hydrochloric acid is among the most strongly dissociated compounds. This is true in general of the salts of ammonia with strong acids. They are nearly as strongly dissociated as the corresponding salts of strong bases like potassium or sodium. A concentrated solution of ammonium chloride is, therefore, a concentrated solution of ammonium ions and chlorine ions. If into such a solution containing a large number of ammonium ions ammonia gas is conducted, the ammonium hydroxide formed will be dissociated far less than in pure water at the same concentration. This could have been predicted from the law of mass action, and what has already been said (p. 318) of the effect of one substance on the solubility of another with a common ion. The presence of ammonium ions diminishes the number of such ions which can be formed from the ammonium hydroxide in the same solution, or, as we say, drives back the dissociation of the ammonium hydroxide.

When ammonium chloride is heated it volatilizes at about 450°. Some of the most interesting phenomena connected with ammonium chloride have to do with the condition of the substance in the form of vapor. When ammonium chloride is volatilized it is dissociated in part into the molecules NH_3 and HCl by heat. The experimental methods by which this is proved have already been discussed (p. 89). The higher the temperature, the greater the amount of the salt broken down into its constituent molecules.

If an excess of either ammonia or hydrochloric acid is present, the dissociation of the ammonium chloride by heat is greatly diminished. Here again we have an example of the influence of mass on chemical activity. If ammonium chloride is volatilized into an atmosphere which contains either of the products of dissociation, NH_3 or HCl, the amount of the dissociation is diminished. This is the same law with which we have already become familiar in connection with phosphorus pentachloride.

The volatilization of ammonium chloride is particularly interesting, in that water plays such a prominent rôle in connection with the dissociation of its vapor. *Dry ammonium chloride is only slightly dissociated into ammonia and hydrochloric acid when volatilized.* The presence of water-vapor accelerates the dissociation of the ammonium chloride. This is just the opposite of what we might expect, since the presence of water is absolutely necessary in order that ammonia gas should combine with hydrochloric acid gas.

Ammonium chloride in water shows a slightly acid reaction. This is due to the hydrolysis of the salt of the weak base ammonia by the water: —

$$NH_4Cl + H_2O = \overset{-}{Cl}, \overset{+}{H} + NH_4OH.$$

Hydrochloric acid being strongly dissociated, while ammonium hydroxide is only weakly dissociated, there are more hydrogen ions in the solution than hydroxl ions, and, consequently, the solution shows an acid reaction.

Ammonium Hydrazoate or Triazoate, N_4H_4. — This salt of hydrazoic acid is remarkable on account of its composition. It contains the same number of hydrogen and nitrogen atoms. It is obviously the ammonium salt of hydrazoic acid: —

$$HN_3 + NH_4OH = H_2O + N_4H_4,$$

or,

$$HN_3 + NH_3 = N_4H_4.$$

As we would expect from its composition, this salt is explosive, and it explodes with violence on account of the large volume of gases which it yields.

$$N_4H_4 = 2\,N_2 + 2\,H_2.$$

This salt is most readily prepared by means of complex organic reactions, which it would lead us too far to take up in detail.

Ammonium Nitrite, NH_4NO_2. — The nitrite is conveniently prepared by the action of ammonium chloride on silver nitrite, insoluble silver chloride being formed: —

$$NH_4Cl + AgNO_2 = AgCl + NH_4NO_2.$$

When ammonium nitrite is heated it breaks down into nitrogen and water: —

$$NH_4NO_2 = 2\,H_2O + N_2.$$

It is of importance, as a means of preparing pure nitrogen. When a solution of ammonium nitrite is heated, nitrogen is given off. In preparing nitrogen in this way, it is only necessary to mix solutions of an ammonium salt and a nitrite and to heat the mixture.

Ammonium Nitrate, NH_4NO_3. — The nitrate of ammonium is formed by the action of ammonium hydroxide on nitric acid: —

$$NH_4OH + HNO_3 = H_2O + NH_4NO_3.$$

The salt is very soluble in water, producing a marked lowering of temperature. The dry salt is decomposed by heat into nitrous oxide and water: —

$$NH_4NO_3 = 2\,H_2O + N_2O.$$

Ammonium nitrate is coming into use as an explosive. It decomposes when quickly heated to a high temperature, yielding water-vapor, nitrogen, and nitric oxide, all of which are gaseous. The volume of the gases set free is thus very great, and its power as an explosive thereby increased. Further, the compound leaves no residue when it explodes, and, therefore, the explosion takes place without any appreciable amount of smoke or solid matter to contaminate the gun. This substance has the further advantage that it is quite stable under ordinary conditions.

Ammonium Hydrosulphide, Sulphide, and Polysulphides.—When a solution of ammonium hydroxide is saturated with hydrogen sulphide, the *hydrosulphide* NH_4HS is produced:—

$$NH_4OH + H_2S = H_2O + NH_4HS.$$

This substance can be obtained in the form of crystals, most readily by allowing ammonia gas and hydrogen sulphide to react in the proper proportions. When volatilized, ammonium hydrosulphide, like ammonium chloride, breaks down into its constituents — ammonia and hydrogen sulphide.

The *sulphide of ammonium*, $(NH_4)_2S$, is formed by treating the hydrosulphide in solution with an equivalent of ammonia:—

$$NH_4HS + NH_4OH = (NH_4)_2S + H_2O.$$

It is also formed by the action of ammonia gas on hydrogen sulphide. Like the hydrosulphide, it can be obtained in the form of a solid, which readily volatilizes. The vapor, like that of ammonium chloride and hydrosulphide, is dissociated by heat into the constituent molecules, ammonia and hydrogen sulphide, as is shown by the abnormally small vapor-density.

The aqueous solution of ammonium sulphide is colorless when freshly prepared, but when allowed to stand for a time it becomes deep-yellow in color. This is due to the oxidation of the sulphide by the oxygen of the air setting sulphur free:—

$$(NH_4)_2S + O = H_2O + 2\,NH_3 + S.$$

The sulphur thus set free acts on more ammonium sulphide, forming the polysulphides of ammonium. There are supposed to be several of these compounds.

Ammonium sulphide is a very useful reagent in qualitative analysis. The sulphides of metals which are soluble in hydrochloric acid are readily thrown down by ammonium sulphide. The polysulphides of ammonium combine with sulphides of arsenic, antimony, gold,

platinum, and tin, and form sulpho-salts. These salts are soluble, and this reagent is therefore useful to dissolve the sulphides of the above five elements and separate them from other substances.

Ammonium Sulphate, $(NH_4)_2SO_4$. — This is one of the most important salts of ammonia, as being one of the chief sources of the ammonia used on a commercial scale. It is readily soluble in water, and is hydrolytically dissociated by it. When heated it yields the acid sulphate: —

$$(NH_4)_2SO = NH_3 + NH_4HSO_4.$$

Ammonium Carbonate, $(NH_4)_2CO_3 . H_2O$. — When a mixture of calcium carbonate and ammonium sulphate is distilled, and ammonia passed into the aqueous solution of the product, normal ammonium carbonate is formed. This is not very stable, and breaks down readily into ammonia and the *acid carbonate*, NH_4HCO_3: —

$$(NH_4)_2CO_3 = NH_3 + NH_4HCO_3.$$

The acid carbonate is also formed by the action of carbon dioxide on aqueous ammonia. This is a much more stable substance than the normal carbonate.

The two carbonates combine, and form what is known as the *sesquicarbonate*, $(NH_4)_2CO_3 . 2\,NH_4HCO_3$. Ammonium carbonate usually contains also the salt of an acid which bears a simple relation to carbonic acid. The salt has the composition, $NH_4CO_2NH_2$, and is known as *ammonium carbamate*. It is obviously ammonium carbonate minus water: —

$$(NH_4)_2CO_3 - H_2O = NH_4CO_2NH_2.$$

Ammonium carbonate is also formed by the action of ammonia gas on carbon dioxide.

Phosphates of Ammonium. — The primary and secondary phosphates of ammonium, $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$, are well-known substances. The tertiary phosphate $(NH_4)_3PO_4$ is probably formed when concentrated ammonia is brought in contact with a concentrated solution of phosphoric acid. It is, however, very unstable, readily losing ammonia and passing over into the secondary phosphate.

When the solution of the secondary phosphate of ammonium is boiled it loses ammonia and passes over into the primary phosphate: —

$$(NH_4)_2HPO_4 = NH_3 + NH_4H_2PO_4.$$

The double phosphate of ammonium and sodium, $NaNH_4HPO_4$, or *microcosmic* salt, has already been referred to (p. 329). When heated it yields sodium metaphosphate: —

$$NH_4NaHPO_4 = H_2O + NH_3 + NaPO_3.$$

Characteristics of the Alkali Metals in General. — From the foregoing study of the alkalies we can draw general conclusions as to their chemical behavior. In the first place, they are all *strongly base-forming elements,* which is the same as to say that when they are dissolved in water they form strongly electro-positive cations, there being a corresponding number of hydroxyl anions present in the solution.

The alkalies form only *univalent ions,* which means that they can carry only one electrical charge. We have already seen that Faraday's law lies at the basis of chemical valence. This can be tested directly in the case of the metals. When a given amount of current is passed through a solution of any alkali chloride, the amount of the corresponding hydroxide formed shows that the cation is univalent. If we insert a solution of a silver salt into the current, and allow the current to flow through this solution and then through the solution of the alkali chloride, we would find that for every gram-atomic weight of silver which separated, a gram-molecular weight of the hydroxide of the alkali would be formed. Since a gram-atomic weight of silver contains the same number of silver ions as a gram-molecular weight of potassium hydroxide contains potassium ions, or a gram-molecular weight of sodium hydroxide contains sodium ions, it follows that an ion of silver carries just the same electrical charge as an ion of potassium or an ion of sodium.

From the law of Faraday, then, all univalent ions carry exactly the same electrical charge. Since it is mainly the ions that react chemically, the question naturally arises, what connection exists between the electrical charges which the ions carry and their chemical behavior. According to our present conceptions, the connection is a very close one. The electrical attraction of these oppositely charged parts, or ions, is undoubtedly an important factor in conditioning chemical union.

This raises one further question. If all the alkalies are univalent, from Faraday's law they all carry the same *amount* of electricity. Is there, then, no difference in the electrical energy carried by a sodium ion from the electrical energy carried by a potassium ion? There may be a marked difference, and this is an important point to note. Electrical energy, like every other form of energy, is made up of two factors, a capacity factor, or *quantity,* and an intensity factor, or *potential.* While the quantity of electricity carried by all univalent ions is the same, the potential of the charge varies from ions of one kind to those of another. This explains why ions of one kind will give up their charge under conditions which would not remove the charge from ions of another element.

The ions of each of the alkali metals have certain characteristic properties which enable them to be distinguished from one another. Some of these have already been referred to. The more important, from the standpoint of analysis, will now be summarized.

The sodium ion forms difficultly soluble compounds with the anion of hydrofluosilicic acid, $\overset{=}{Si}F_6$, and the anion of pyroantimonic acid, $H_2\overset{=}{Sb}_2O_7$.

The potassium ion forms difficultly soluble compounds with the anion of chlorplatinic acid, $P\overset{=}{t}Cl_6$; with the anion of perchloric acid, $\overset{-}{Cl}O_4$; with the anion of hydrofluosilicic acid, $\overset{=}{Si}F_6$; with the anion of tartaric acid, $H(C_4\overset{-}{H}_4O_6)$, and with the cobaltinitrite ion, $Co\overset{\equiv}{(}NO_2)_6$.

The lithium ion forms difficultly soluble compounds with the anion of carbonic acid, $\overset{=}{CO}_3$, and with the anion of phosphoric acid, $\overset{\equiv}{PO}_4$.

The ammonium ion forms difficultly soluble compounds with the anion of chlorplatinic acid, $P\overset{=}{t}Cl_6$; with the anion of tartaric acid, $H\overset{-}{C}_4H_4O_6$, and with the cobaltinitrite ion, $Co(\overset{\equiv}{N}O_2)_6$.

The flame-tests for these several elements were considered when each element was studied in some detail.

CHAPTER XXX

THE ALKALINE EARTHS

CALCIUM, STRONTIUM, BARIUM

CALCIUM (At. Wt. = 40.1)

The metals which we have thus far studied are all univalent, or their ions carry one electrical charge each. In the second group of the metals the ions are nearly always bivalent, and in the calcium, strontium, barium sub-group they are always bivalent. The salts which these elements form with the anions of acids are of the general type MCl_2, $M(NO_3)_2$, MSO_4, MCO_3, $M_3(PO_4)_2$ and so on. With this conception in mind we may now proceed to study in some detail the compounds formed by the several members of the group.

Occurrence, Preparation, and Properties of Calcium. — Calcium occurs very widely distributed in nature and in large quantities. The carbonate occurs in great abundance as *marble* if well crystallized and pure, or if impure as *limestone* or *chalk*. If in combination with magnesium carbonate we have dolomite. Calcium phosphate occurs in considerable quantity in certain phosphate beds. *Gypsum*, or calcium sulphate, occurs in considerable quantity, while calcium fluoride, or *fluor-spar*, exists in certain localities. Calcium comes next to aluminium and iron in the order of abundance in the earth.

Calcium is best prepared by decomposing the iodide by metallic sodium: —

$$CaI_2 + 2\,Na = 2\,NaI + Ca.$$

Calcium is a silvery-white metal, which decomposes water slowly at ordinary temperatures. It combines with the oxygen of the air, and also with the halogens at elevated temperatures. It melts in a vacuum at 760°.

Calcium Hydride, CaH_2. — This compound is formed by the action of hydrogen on hot calcium. Barium and strontium form similar compounds.

Calcium Oxide, or Lime, CaO. — Calcium combines with oxygen, forming the oxide, CaO. This is most conveniently prepared by heating the carbonate: —

$$CaCO_3 = CO_2 + CaO.$$

Calcium oxide is a white, amorphous powder, which is extensively used in a number of chemical operations. It is used as a carrier of chlorine in the form of bleaching-powder, and in general wherever a cheap base is desired. It also acts chemically upon various rocks and minerals in the soil, liberating their constituents in soluble form, so that they can be taken up by the plants.

Calcium oxide does not melt until a very high temperature is reached (about 3000°). It is, therefore, used in constructing the *Drummond light.* When the flame from the oxyhydrogen blowpipe is allowed to play upon a cylinder of lime, it becomes highly heated and at this high temperature gives out an enormous amount of light. It resembles in this respect the oxides of thorium and cerium used in the Welsbach light, the latter, however, giving out large amounts of light energy at a much lower temperature.

When lime is brought in contact with moisture it takes up water and forms calcium hydroxide:—

$$CaO + H_2O = Ca(OH)_2.$$

This process is known as *slaking.*

Calcium Hydroxide or Slaked Lime, $Ca(OH)_2$. — When lime or calcium oxide is thrown into water a large amount of heat is evolved, and calcium hydroxide is formed as stated above. This is a white powder, soluble in water only to the extent of 0.002 part in one part of water. This is known as *lime water.* A mechanical suspension of the finely divided calcium hydroxide in water is known as *milk of lime.*

Calcium hydroxide is a strongly dissociated compound, as is shown by the following molecular conductivities. It dissociates thus: —

$$Ca(OH)_2 = \overset{++}{Ca}, \overset{-}{O}H, \overset{-}{O}H.$$

v	μ_v (25°)
64	381
128	440
256	419
512	427

Its solution contains a large number of hydroxyl ions, and it is, therefore, a very strong base. It is, however, not quite as strongly dissociated as the hydroxides of the alkalies. When a clear solution of calcium hydroxide is allowed to stand exposed to the air for a short time, it takes up carbon dioxide from the air, forming flakes of the insoluble calcium carbonate: —

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$

When lime is exposed to the air the same reaction takes place to some extent. The calcium oxide takes up moisture from the air, forming the hydroxide, and this combines in part with carbon dioxide, forming the carbonate. The white powder formed when lime is exposed to the air, known as *air-slaked lime*, is, then, a mixture of calcium oxide and calcium carbonate. Lime mixed with caustic soda is known as *soda-lime.*

Compounds of Calcium with the Halogens. — Calcium combines with the halogens, forming compounds of the general type CaA_2, where A represents a halogen anion.

The *chloride*, $CaCl_2 . 6\,H_2O$, is very soluble in water, producing when dissolved a considerable lowering of temperature. By mixing this salt in the proper proportions with finely powdered ice, a temperature as low as $-30°$ to $-35°$ can be produced. The salt is most readily prepared by dissolving marble, which is pure calcium carbonate, in hydrochloric acid, and evaporating the solution to crystallization. The salt when heated loses water, and if highly heated hydrochloric acid, forming calcium oxide. When heated in an atmosphere of dry hydrochloric acid gas all of the water can be removed from calcium chloride without the salt undergoing any decomposition.

On account of its attraction for water, anhydrous calcium chloride is frequently used as a drying agent, especially for gases. These are passed slowly through tubes filled loosely with calcium chloride, and most of the water is removed from the gases and absorbed by the chloride. Calcium chloride, however, does not remove all of the water from substances. Indeed, it is not as good a drying agent as sulphuric acid, and still less than phosphorus pentoxide, which is the best drying agent known to the chemist. Calcium chloride, however, cannot be used at all to dry ammonia gas, since it combines with ammonia, forming definite compounds, such as $CaCl_2 . 4\,NH_3$, and $CaCl_2 . 8\,NH_3$.

Calcium bromide, $CaBr_2$, and *calcium iodide*, CaI_2, present few points requiring special comment. They are not very stable compounds, the iodide especially breaking down in the presence of the oxygen and carbon dioxide in the air, yielding free iodine.

Calcium fluoride, CaF_2, or fluor-spar, is a beautifully crystalline substance, practically insoluble in water, and is the chief source of hydrofluoric acid and fluorine. Many varieties of fluor-spar are strongly *fluorescent*, *i.e.* have the power of lengthening the wave-lengths of the light which is allowed to fall upon them.

Calcium Hypochlorite Bleaching-powder, $Ca(OCl)_2$. — When chlorine is conducted into lime it is absorbed by the lime. The reaction which takes place may be represented thus: —

$$(1) \qquad 2\,Ca(OH)_2 + 2\,Cl_2 = CaCl_2 + Ca(OCl)_2 + 2\,H_2O,$$

giving a mixture of calcium chloride and hypochlorite; or it may be represented thus: —

$$(2) \qquad 2\,Ca(OH)_2 + 2\,Cl_2 = 2\,Ca<^{OCl}_{Cl} + 2\,H_2O,$$

forming one compound, which is half chloride and half hypochlorite.

It is difficult to decide between these two possibilities. The fact that bleaching-powder is not deliquescent, while calcium chloride is strongly deliquescent, would indicate that there is no calcium chloride in bleaching-powder. In aqueous solution the two reactions would obviously yield exactly the same ions: —

$$(1) \qquad CaCl_2 + Ca(OCl)_2 = \overset{++}{Ca},\ \overset{-}{Cl},\ \overset{-}{Cl}, + \overset{++}{Ca},\ \overset{-}{OCl},\ \overset{-}{OCl},$$

$$(2) \qquad 2\,Ca<^{Cl}_{OCl} = \overset{++}{Ca},\ \overset{-}{Cl},\ \overset{-}{Cl} + \overset{++}{Ca},\ \overset{-}{OCl},\ \overset{-}{OCl}.$$

The difficulty in deciding between equations (1) and (2) is thus apparent. All things considered, however, it seems probable that bleaching-powder is a definite chemical composed of the composition expressed by the formula $Ca<^{OCl}_{Cl}$.

When treated with an acid, bleaching-powder gives up all of its chlorine.

$$Ca<^{OCl}_{Cl} + 2\,HCl = CaCl_2 + H_2O + Cl_2,$$

$$Ca<^{OCl}_{Cl} + H_2SO_4 = CaSO_4 + H_2O + Cl_2.$$

Bleaching-powder is thus a very convenient means of transporting chlorine without loss, since all the chlorine which was taken up by the lime is set free when the bleaching-powder is treated with an acid. This chlorine can be used for bleaching or for antiseptic purposes. When bleaching-powder is exposed to the air it always has the odor of chlorine. This is due to the action of the carbon dioxide in the air, forming calcium carbonate and liberating chlorine.

$$Ca<^{OCl}_{Cl} + CO_2 = CaCO_3 + Cl_2.$$

Calcium carbonate, being a stable solid not very soluble in water, is formed.

When bleaching-powder is heated it forms calcium chlorate and calcium chloride: —

$$6\,Ca{<}^{OCl}_{Cl} = Ca(ClO_3)_2 + 5\,CaCl_2.$$

Calcium chlorate can be used as the starting-point in preparing potassium chlorate.

When bleaching-powder is brought together with certain compounds rich in oxygen, like hydrogen dioxide, it gives up oxygen: —

$$Ca{<}^{OCl}_{Cl} + H_2O_2 = H_2O + CaCl_2 + O_2.$$

Half of the oxygen set free comes from the dioxide and half from the bleaching-powder. This is the most convenient method of determining the strength of a solution of bleaching-powder.

Sulphides of Calcium. — *Calcium Hydrosulphide*, $Ca(SH)_2$, is formed when hydrogen sulphide is conducted into a solution of calcium hydroxide: —

$$Ca(OH)_2 + 2\,H_2S = Ca(SH)_2 + 2\,H_2O.$$

This salt, which is also formed when calcium sulphide dissolves in water, —

$$2\,CaS + 2\,H_2O = Ca(OH)_2 + Ca(SH)_2,$$

has never been isolated from the solution. When an attempt is made to obtain it, hydrogen sulphide is given off and *calcium sulphide* remains behind: —

$$Ca(SH)_2 = H_2S + CaS.$$

Calcium sulphide was supposed for a long time to have the power of emitting light in the dark, or to be *luminescent* or *phosphorescent.* This property has been shown to be due to the presence of small quantities of the sulphides of certain metals, such as manganese.

Calcium Sulphate, $CaSO_4$. — The sulphate of calcium containing two molecules of water of crystallization, and known as *gypsum* — $CaSO_4.2\,H_2O$ — occurs abundantly in nature. It dissolves in water to some extent, 2 parts in 1000, and is frequently found in solution. It also occurs in the solid form in many localities.

Gypsum is useful chiefly on account of the transformations which take place when its water is removed by heat, and the anhydrous salt is brought again into contact with water. When gypsum is heated to 107° it loses one and a half molecules of water: —

$$CaSO_4.2\,H_2O = CaSO_4.\tfrac{1}{2}\,H_2O + 1\tfrac{1}{2}\,H_2O,$$

or,

$$2\,CaSO_4.2\,H_2O = 2\,CaSO_4.H_2O + 3\,H_2O.$$

Gypsum which is thus partially dehydrated is a flowery powder, and is known as *plaster of paris*. When brought in contact with water, plaster of paris takes it up again and forms gypsum. The mass, however, is now finally divided, and hardens after a few minutes. It is used extensively for making mouldings and casts of objects, especially of marble statuary.

If the temperature to which the gypsum is heated is at all high (200°), it loses all of its water. When the completely dehydrated product is brought in contact with water it combines with the water very slowly, and is useless as far as making mouldings is concerned. Such gypsum is known as "hard burned" or "dead burned" gypsum.

Calcium sulphate occurs in nature also in the anhydrous form. In this condition it is known as *anhydrite*, and usually occurs in the salt-beds deposited from seas which have evaporated. It can be prepared by fusing together calcium chloride and potassium sulphate: —

$$CaCl_2 + K_2SO_4 = 2\,KCl + CaSO_4.$$

Calcium Carbide, CaC_2. — Calcium carbide has come into very great prominence recently on account of its method of preparation, and because when brought into the presence of water it readily yields the illuminant acetylene.

The carbide of calcium is prepared by heating a mixture of finely divided carbon and lime in an electric furnace: —

$$3\,C + CaO = CO + CaC_2.$$

Calcium carbide has been prepared in the form of transparent crystals. The product as it comes on the market is a grayish solid, which, when exposed to the air has the odor of acetylene.

Its commercial value depends entirely upon the fact that it decomposes with water, giving acetylene gas: —

$$CaC_2 + H_2O = CaO + C_2H_2.$$

Acetylene gas has recently come into great prominence as an illuminant. This is due to the ease with which it can be made from calcium carbide. Water is admitted slowly to the carbide when the acetylene is desired, and a slow or rapid current of the gas generated at will.

Calcium Carbonate, $CaCO_3$. — The most abundant and important compound of calcium which occurs in nature is the carbonate *calcite*. It occurs in beautifully transparent, crystalline masses in Iceland, and is known as *Iceland spar*. Another crystalline variety of calcium car-

bonate is *aragonite.* This crystallizes in a different crystallographic system from Iceland spar, and we therefore have *diamorphism* represented by calcium carbonate. When aragonite, which is orthorhombic, is heated, it passes over into hexagonal Iceland spar. The latter is, therefore, the stable, the former the metastable, phase. We have here a case somewhat analogous to those already met with in oxygen, sulphur, phosphorus, etc., and it is probable that the two forms of calcium carbonate contain different amounts of intrinsic energy in their molecules.

Calcium carbonate occurs in great abundance in less beautifully crystallized condition. *Marble* is a crystallized form of calcium carbonate. *Limestone* is also calcium carbonate and is usually crystalline, but the crystals are generally smaller than in marble and are contaminated with various impurities. *Chalk* is a very fine-grained variety of calcium carbonate, formed chiefly of the shells of microscopic organisms. Indeed, calcium carbonate is frequently of organic origin, consisting of shells of animals which have been more or less metamorphosed by the geological processes to which they have been subjected.

Calcium carbonate can be readily formed in the laboratory by treating a soluble calcium salt with a soluble carbonate: —

$$CaCl_2 + Na_2CO_3 = 2\,NaCl + CaCO_3,$$

$$Ca(NO_3)_2 + K_2CO_3 = 2\,KNO_3 + CaCO_3.$$

When calcium carbonate is heated it undergoes decomposition into lime and carbon dioxide, as we saw when we were studying lime: —

$$CaCO_3 = CaO + CO_2.$$

At a given temperature this decomposition takes place until the carbon dioxide acquires a certain pressure. When this pressure is reached the carbon dioxide combines as rapidly with the lime to reform calcium carbonate as the latter decomposes. The pressures of carbon dioxide at which equilibrium exists for several temperatures are given below: —

Temperatures	Pressures of Carbon Dioxide
610°	4.6 millimetres of Hg
740°	25.5 millimetres of Hg
810°	67.8 millimetres of Hg
865°	133.3 millimetres of Hg

If we plot these results in a curve it will have the form represented in Fig. 36. We have two components, carbon dioxide and lime, and three phases, carbon dioxide, lime, and calcium carbonate. We have, from the phase rule, one degree of freedom, and can vary either the temperature or pressure along the curve without destroying the equilibrium.

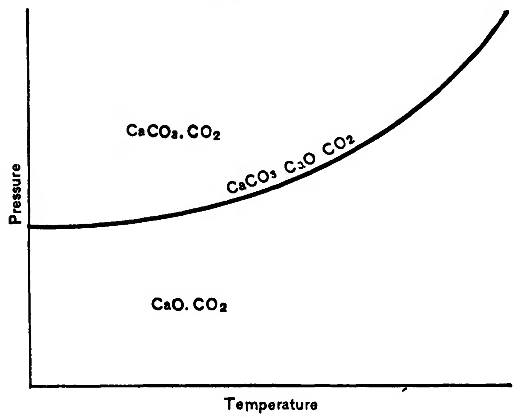


FIG. 36.

As has already been stated, lime is used extensively in agriculture. It is also used extensively in architecture, as *mortar*, for holding together bricks and stone. Mortars are made by mixing calcium hydroxide and sand in the presence of enough water to form a pasty mass. This is placed beneath each brick or stone, upon the brick or stone below, and then allowed to harden as it is said. The lime is in the form of the hydroxide. When this comes in contact with the carbon dioxide in the air it is retransformed into carbonate: —

$$Ca(OH)_2 + CO_2 = H_2O + CaCO_3,$$

and this is the chemical process which takes place when mortar hardens. There is a large amount of water given off in the sense of the above equation, and this agrees with universal experience that a house which is freshly plastered is always damp. The hardening or setting of mortar could be effected much more rapidly by exposing it to an atmosphere rich in carbon dioxide, as by generating large amounts of carbon dioxide in rooms which had been freshly plastered.

When limestone, containing as impurities clay and magnesium carbonate, is heated, the product forms with water a very hard mass. This is known as *hydraulic cement.*

Portland cement is made either from a mixture of pure calcium carbonate and clay, or from marl, which is a mixture of silicates and calcium carbonate.

Calcium carbonate is not readily soluble in pure water, but dissolves to a very considerable extent in water containing carbon dioxide.

Primary or Acid Calcium Carbonate, $Ca(HCO_3)_2$, is formed when the normal carbonate is dissolved in water containing carbon dioxide: —

$$CaCO_3 + H_2O + CO_2 = Ca(HCO_3)_2.$$

Into water containing normal calcium carbonate in suspension conduct a current of carbon dioxide, and the calcium carbonate will pass into solution as the acid carbonate. The acid carbonate cannot, however, be isolated. Indeed, when its solution is boiled the acid carbonate is decomposed into the normal carbonate and carbon dioxide is given off.

When a solution of the acid carbonate is evaporated at ordinary temperatures the normal carbonate is deposited. This is the way in which the *stalagma* in caverns are formed. The waters containing acid calcium carbonate in solution percolate through the roof of a cavern, and evaporating, deposit calcium carbonate on the ceiling. This continues, the solution of the carbonate trickling over the outside of the deposit already formed, until frequently very beautiful hanging columns result. Such formations suspended from the ceiling or sides of a cavern are called *stalactites.* The solution of the carbonate frequently drops off of the stalactite, since the rate of evaporation in a closed space beneath the surface of the earth must be very slow. Where it drops on the floor of the cavern it evaporates and deposits its carbonate, and we frequently find columns and pillars of calcium carbonate growing upward from the floor of caverns. Such growths are known as *stalagmites.* It not infrequently happens that the stalactite grows downward and the stalagmite upward until the two meet, and continuous columns result. The beautiful and fantastic decorations of many caverns is to be traced, then, to the action of water containing carbon dioxide on calcium carbonate, resulting in the formation of the acid carbonate, which is fairly soluble. This is true in caverns like Luray in Virginia, while the stalagma in the Mammoth Cave of Kentucky are mainly gypsum.

Natural waters frequently contain carbon dioxide in considerable quantity. This is produced by decomposing vegetable matter in the soil through which they percolate, and is also taken from the atmospheric air. Consequently, many natural waters contain calcium carbonate in solution. Such are known as *hard waters.*

Where the hardness is due to the presence of acid calcium carbonate this is removed by boiling the water, the acid carbonate being decomposed, as we have seen, into the normal carbonate which is precipitated, and carbon dioxide which is set free. Such waters are known as *temporarily hard.*

Waters not infrequently contain in solution other salts of calcium, as the sulphate, and also the salts of other metals. When such water is boiled these salts are not precipitated, and hence such waters are *permanently hard.*

Phosphates of Calcium. — The three calcium salts of phosphoric acid are all known. They are the normal salt, $Ca_3(PO_4)_2$, the secondary salt, $CaHPO_4$, and the primary salt, $CaH_4(PO_4)_2$.

Tricalcium phosphate, $Ca_3(PO_4)_2$, is found in large quantity in the bones of animals, and is therefore very important in connection with animal life. When bones are heated to a high temperature in contact with the air the organic matter is destroyed, and the calcium phosphate and other mineral matter in the bones remain behind in the *bone-ash.*

The normal calcium phosphate also occurs in nature as *phosphorite,* in combination with chloride or fluoride as *apatite;* and in addition large beds of phosphate rock which are mainly of animal origin occur in certain regions of the world, especially in the southern parts of the United States, in Georgia, Florida, South Carolina, and Tennessee.

The phosphoric ions — tertiary, secondary, and primary, $\overset{\equiv}{P}O_4$, $H\overset{=}{P}O_4$ or $H_2\overset{-}{P}O_4$ — are of fundamental importance for the growth, and especially for the seeding, of certain plants and grasses. Among these are the very valuable cereals wheat and corn. These plants gradually remove the phosphoric acid ion from the soil, and the latter would soon become impoverished in this substance, were it not supplied to the soil artificially. The most important constituent of commercial fertilizer is phosphoric acid ions. These, however, are not supplied in the form of the tricalcium phosphate, since this salt is not sufficiently soluble in water.

We shall see that normal calcium phosphate is readily transformed into calcium phosphates which are soluble in water.

Normal calcium phosphate is formed when a soluble calcium salt is added to a solution of disodium phosphate containing ammonia: —

$$3\,CaCl_2 + 2\,Na_2HPO_4 + 2\,NH_3 = 4\,NaCl + 2\,NH_4Cl + Ca_3(PO_4)_2.$$

When the normal calcium phosphate is treated with an acid it readily dissolves. If the acid is weak the secondary salt is formed; if it is strong the primary salt is produced.

Secondary calcium phosphate, $CaHPO_4$, is formed by the action of a soluble calcium salt on disodium phosphate in the presence of a little acid. If no acid is added the tricalcium phosphate is first formed, but since in this reaction acid is formed, this acid reacts

slowly on the triphosphate, converting it into the secondary phosphate: —

$$2\,Na_2HPO_4 + 3\,CaCl_2 = Ca_3(PO_4)_2 + 4\,NaCl + 2\,HCl,$$
$$Ca_3(PO_4)_2 + 2\,HCl = CaCl_2 + Ca_2H_2(PO_4)_2.$$

In this reaction we pass from the trivalent phosphoric ion $\overset{\equiv}{PO_4}$, to the divalent, secondary, phosphoric ion $\overset{=}{HPO_4}$.

If a little acetic acid is added to the solution of disodium phosphate and calcium chloride then introduced, the tricalcium phosphate is formed at once: —

$$3\,CaCl_2 + 2\,Na_2HPO_4 + (CH_3COOH) = Ca_3(PO_4)_2 + 4\,NaCl + 2\,HCl.$$

If tricalcium phosphate is treated with a strong acid, *i.e.* with a concentrated solution of hydrogen ions in the proper proportion, the *primary calcium phosphate* is formed: —

$$Ca_3(PO_4)_2 + 2\,H_2SO_4 = 2\,CaSO_4 + CaH_4(PO_4)_2.$$

This is the commercial "superphosphate." In the presence of iron or aluminium compounds it *reverts*, as it is said, probably forming aluminium and ferric phosphates.

In preparing *commercial fertilizer* the tertiary calcium phosphate is the starting-point in obtaining phosphoric acid ions. Although this is acted upon slowly by the carbonic acid, and organic acids formed from decomposing vegetable matter in the soil, and converted into the more acid phosphates which are soluble in water, this process is too slow to secure the best results.

The tricalcium phosphate in ground bone, or in finely ground phosphate rock, is treated with sulphuric acid and converted into the secondary and primary phosphates, which are somewhat soluble in water. This is known as "soluble or available" phosphoric acid, while the phosphoric acid in the form of tricalcium phosphate is known as "insoluble" phosphoric acid.

In *analyzing a commercial phosphate* a given amount of the salt is treated with a given amount of water at a given temperature, and shaken for a given length of time. The phosphoric acid dissolved by the water can then be determined by precipitating with ammonium molybdate, dissolving in ammonia, and precipitating with the "magnesia mixture" as ammonium magnesium phosphate. This is heated and weighed as magnesium pyrophosphate. This is known as "water soluble" phosphoric acid. The residue is then treated with a given amount of a standard solution of ammonium citrate, in which the secondary calcium phosphate is soluble. This is known as "citrate soluble" phosphoric acid. The part of the phosphoric

acid insoluble in water and ammonium citrate is in combination with calcium, as tricalcium phosphate, and is known as "insoluble" phosphoric acid. The "water soluble" plus the "citrate soluble" phosphoric acid are known as the "available phosphoric acid."

Calcium Silicate, $CaSiO_3$. — The silicate of calcium occurs in nature as *wollastonite.* It also occurs with other silicates in such well-known minerals as *mica* and *garnet.* Its chief importance is in connection with the manufacture of *glass.* Glass is, in general, an amorphous mixture of the silicate of calcium with the silicates of the alkalies. There are a number of varieties of glass, and a few of these will be reconsidered.

Glass is made by fusing together sand, calcium carbonate, and the carbonate of the alkali desired. If sodium carbonate is used we have soda glass, if potassium carbonate is employed, potash glass, etc.

Soda glass is prepared by fusing together sodium carbonate, calcium carbonate, and silicon dioxide. Soda glass is readily fusible, and is easily attacked by chemical reagents such as boiling alkalies. It is blown into cylinders, which are then opened and flattened, and cut into ordinary window panes. This is known as "soft glass," because it is easily worked in the blast-lamp, and has applications in the chemical laboratory, although, on account of its solubility it is not well adapted for bottles for holding chemical reagents.

Bohemian or potassium glass is a potassium calcium silicate. It is much harder than the soda glass, fuses at a much higher temperature, and is much more resistant to chemical reagents. It is, therefore, valuable to the chemist, and is extensively employed in the manufacture of apparatus which is to be heated to a high temperature, such as combustion-tubing and the like.

Flint-glass consists of potassium and lead silicates, the lead taking the place of calcium in ordinary soda or potassium glass. It has such a high refractive power that it is used in making optical lenses.

Thallium flint-glass contains thallium instead of potassium, and has still higher refractivity and greater dispersion than ordinary flint-glass.

Strass is a silicate of lead, potassium, and sodium, and also contains some boric acid. It has such high refractivity that it is used in making imitation gems.

The *colored glasses* are prepared by adding to the fused silicates oxides of certain metals which give the desired color to the glass. *Yellow glasses* owe their color to uranium or antimony; *blue glasses* to cobalt and manganese, *red glasses* to copper, iron, or sometimes gold, *green glasses* to chromium or copper, and so on. Glasses of almost

every shade of color have been prepared by using different coloring constituents or mixtures of these constituents.

Most of the glass objects with which we are ordinarily familiar are *blown.* A large ball of molten glass is taken on the end of a hollow metal tube, through which the breath can be blown. The tube is then moved rapidly backwards and forwards through the air beneath the glass blower, who drives air through the tube at the desired rate and time. The glass takes the form usually of a hollow cylinder, which is blown out to the desired thickness. This is cracked, flattened, and cut into the desired size. In this way flat panes of glass are made. Bottles are blown into moulds, and other glass objects of definite shape are either blown into moulds or moulded. Such objects must be *annealed.*

The property of the glass is largely conditioned by the way in which it is annealed. If glass is cooled with moderate rapidity it has the properties which we ordinarily associate with it. If cooled very rapidly, however, it has very different properties. It is under a considerable strain, and when the surface is fractured in any way, the glass flies in pieces almost with explosive violence. The *Prince Rupert drops*, made by dropping molten glass into water, are examples of this condition.

On the other hand, when glass is cooled very slowly, as by introducing it when hot into hot oil, or by placing it in an oven which is cooled slowly, it is much less easily broken than ordinary glass. It acquires considerable elasticity, and can be struck a fairly hard blow without injury.

Calcium Oxalate, CaC_2O_4. — We have already studied a number of salts of calcium which are practically insoluble in water. These include the phosphate, carbonate, and, to some extent, the sulphate. Another compound of calcium, which is only slightly soluble in pure water, is calcium oxalate — the calcium salt of the dibasic, organic acid $H_2C_2O_4$. When a solution of any calcium salt is treated with a solution of ammonium oxalate, calcium oxalate is precipitated: —

$$CaCl_2 + C_2O_4(NH_4)_2 = 2\,NH_4Cl + CaC_2O_4.$$

Ammonium oxalate is used to precipitate calcium oxalate and not free oxalic acid, since calcium oxalate is soluble in strong acids. If free oxalic acid were used in the above case, instead of ammonium oxalate, hydrochloric acid would be liberated, and this would redissolve the oxalate. Oxalic acid is a dibasic acid, and the above equation should be written: —

$$\overset{++}{Ca},\ \overset{-}{Cl},\ \overset{-}{Cl} + \overset{+}{N}H_4,\ \overset{+}{N}H_4,\ C_2\overset{=}{O}_4 = \overset{+}{N}H_4,\ \overset{-}{Cl} + \overset{+}{N}H_4,\ \overset{-}{Cl} + CaC_2O_4.$$

Calcium is frequently precipitated as the oxalate in quantitative determinations of this element. The oxalate loses more and more water of crystallization as the temperature is raised, and is, therefore, not a good salt to weigh. The oxalate is easily decomposed to the oxide, which is the form in which the calcium is most conveniently weighed: —

$$CaC_2O_4 = CaO + CO + CO_2.$$

It may also be decomposed into the carbonate by careful heating, and the carbonate then converted into the oxide: —

$$CaC_2O_4 = CaCO_3 + CO.$$

Detection of Calcium. — In addition to the insoluble compounds formed by calcium, the spectroscope furnishes a valuable means of detecting calcium. When a calcium salt is introduced into the colorless flame of a Bunsen burner, the flame is colored orange-red, and can easily be recognized with a little practice. If examined with the spectroscope the calcium flame shows a heavy line in the orange-red, another in the green, and a still fainter line in the blue.

STRONTIUM (At. Wt. = 87.6)

The element strontium resembles calcium very closely in its properties and in the properties of its compounds. It will, therefore, be treated very briefly, certain differences between the two being pointed out.

Occurrence, Preparation, and Properties of Strontium. — Strontium occurs in nature chiefly in the form of two salts which are well-known minerals. These are strontium carbonate or *strontianite*, and strontium sulphate or *celestite*.

The element is prepared most conveniently by electrolyzing the fused chloride, the metal separating at the cathode.

Strontium resembles calcium in its appearance and properties. It has a yellowish tint, combines with the oxygen of the air, acts upon water setting hydrogen free and forming the hydroxide, and in general so closely resembles calcium that it is unnecessary to describe its properties in detail.

Salts of Strontium. — Strontium forms the divalent ion $\overset{++}{Sr}$, which is strictly analogous to the calcium ion $\overset{++}{Ca}$. It combines with two hydroxyl ions forming *strontium hydroxide*, $Sr(OH)_2$, whose aqueous solution is strongly basic. This substance is more soluble in water than calcium hydroxide, and crystallizes from the aqueous solution with eight molecules of water: $Sr(OH)_2.8\,H_2O$. *Strontium nitrate*,

$Sr(NO_3)_2$, like strontium salts in general, gives a beautiful red color to a colorless flame. It is used, because of this property, to produce red light in fireworks and other pyrotechnic displays. Strontium nitrate is insoluble in alcohol, and thus differs from calcium nitrate, which dissolves readily in this solvent. This fact is made use of to separate strontium from calcium.

The strontium ion combines with the anions of acids, forming in general the same insoluble compounds as calcium. Certain differences in the degree of solubility however, manifest themselves. Strontium combines with the carbonic ion $\overset{=}{CO_3}$ forming *strontium carbonate*, $SrCO_3$. As already stated, this occurs in nature as the mineral strontianite, and is the source of the element strontium. It is practically insoluble in water and is, therefore, precipitated when a soluble carbonate is added to a soluble strontium salt: —

$$Na_2CO_3 + SrCl_2 = 2\,NaCl + SrCO_3.$$

Strontium carbonate dissolves readily in hydrochloric or nitric acid, forming the corresponding chloride or nitrate. It is difficult to decompose strontium carbonate, a very high temperature being required.

The *chloride* contains six molecules of water of crystallization, $SrCl_2 . 6\,H_2O$. It readily takes up water from the air but not as readily as calcium chloride. Strontium chloride is easily soluble in alcohol, and thus differs from barium chloride, which is insoluble in this solvent.

Strontium combines with the sulphuric ion $\overset{=}{SO_4}$, forming *strontium sulphate*, $SrSO_4$. This salt occurs in nature as *celestite*, and since it is only slightly soluble in water, is formed when a soluble sulphate is added to a soluble strontium salt: —

$$Na_2SO_4 + SrCl_2 = 2\,NaCl + SrSO_4.$$

Strontium sulphate is much less soluble in water than calcium sulphate, and is practically insoluble in a mixture of water and alcohol.

The strontium ion forms difficultly soluble compounds also with the ions $\overset{\equiv}{PO_4}$ and $H\overset{=}{PO_4}$. The normal *phosphate*, $Sr_3(PO_4)_2$, and *secondary phosphate*, $SrHPO_4$, are quite insoluble. With the ion of oxalic acid, $\overset{=}{C_2O_4}$, the strontium ion combines, forming insoluble *strontium oxalate*, SrC_2O_4.

The *chromate of strontium*, $SrCrO_4$, is fairly soluble.

Detection of Strontium. — Strontium is easily detected by the color which it imparts to the flame. It produces an intensely dark-

red flame, which can be easily recognized. When this flame is examined with the spectroscope it is found to contain a number of lines in the red and orange-red, and one characteristic line in the blue. Since strontium is the only common substance which gives a deep-red flame, its presence is usually detected by the flame reaction alone. Methods of separating it from calcium and barium will be considered a little later.

BARIUM (At. Wt. = 137.4)

An element closely allied to calcium and strontium is barium. This element occurs chiefly as the sulphate, $BaSO_4$, which is known as *barite* or *heavy spar*, and as the carbonate, $BaCO_3$, known as *witherite*.

Barium, like strontium and calcium, is prepared by electrolyzing the fused chloride. The metal barium is white, takes up oxygen from the air, and decomposes water with evolution of hydrogen. The reaction with water is more vigorous than that of calcium or strontium, and in this it more closely resembles the alkalies.

Oxides of Barium. — Barium forms two oxides — the normal oxide, BaO, and the dioxide, BaO_2. *Barium oxide*, BaO, is formed by heating the nitrate.

$$2\,Ba(NO_3)_2 = 2\,BaO + 4\,NO_2 + O_2.$$

It can be prepared from the carbonate, not conveniently, however, by heating directly, since the carbonate decomposes only when heated to a very high temperature. It can, however, be readily prepared by heating the carbonate with carbon: —

$$BaCO_3 + C = 2\,CO + BaO.$$

Barium dioxide, BaO_2, is formed by heating the oxide to 500° in a current of air or oxygen: —

$$2\,BaO + O_2 = 2\,BaO_2.$$

Barium dioxide is an excellent "carrier of oxygen," since at a somewhat higher temperature it gives up its excess of oxygen and forms barium oxide again: —

$$2\,BaO_2 = 2\,BaO + O_2.$$

We have already become familiar with this substance in connection with the preparation of hydrogen dioxide. When it is treated with an acid the following reaction takes place: —

$$BaO_2 + 2\,HCl = BaCl_2 + H_2O_2.$$

With water, barium dioxide forms the hydrate with eight molecules of water of crystallization — $BaO_2 . 8\,H_2O$.

Barium Hydroxide, $Ba(OH)_2$. — The hydroxide of barium is formed when the oxide is dissolved in water, $BaO + H_2O = Ba(OH)_2$. Barium oxide is much more soluble in water than strontium oxide, which in turn is more soluble than calcium oxide.

The hydroxide of barium crystallizes in beautiful, white plates, containing eight molecules of water — $Ba(OH)_2 . 8\,H_2O$.

The hydroxide is readily soluble in water, especially at an elevated temperature. It dissolves in three parts of boiling water and in twenty parts of cold water; a solution saturated when hot, therefore, crystallizes out in abundance when cooled. A solution of barium hydroxide in water is known as *baryta water*. This solution is strongly basic, showing that barium hydroxide readily dissociates thus: —

$$Ba(OH)_2 = \overset{++}{Ba}, \overset{-}{OH}, \overset{-}{OH}.$$

This is shown by the large values of its conductivities.

v	μ_v (25°)
8	349
64	402
512	437
1024	440

As a strong base it is frequently used to neutralize acids, and to standardize solutions of acids by titration, using some of the indicators already studied to determine when the neutralization is just complete. A solution of baryta water is frequently used to detect the presence of carbon dioxide. On account of the insolubility of barium carbonate, a minute trace of carbon dioxide can be detected by means of this reagent: —

$$Ba(OH)_2 + CO_2 = BaCO_3 + H_2O.$$

Barium Chloride, $BaCl_2 . 2\,H_2O$ — The chloride of barium is formed by dissolving the carbonate (witherite) in hydrochloric acid: —

$$BaCO_3 + 2\,HCl = H_2O + CO_2 + BaCl_2.$$

Also by treating barium sulphide with magnesium chloride and water: —

$$BaS + MgCl_2 + 2\,H_2O = H_2S + Mg(OH)_2 + BaCl_2.$$

Barium chloride is less soluble in water than strontium chloride, which is less soluble than calcium chloride. This is exactly the reverse of the solubilities of the oxides, barium oxide being the most soluble, strontium oxide less soluble, and calcium oxide the least soluble of the three.

Barium Sulphate, $BaSO_4$. — The sulphate of barium, or *heavy spar*, occurs in nature as stated above. It is readily formed whenever a soluble sulphate is added to a soluble barium salt: —

$$Ba(NO_3)_2 + K_2SO_4 = 2\,KNO_3 + BaSO_4.$$

It is the most insoluble sulphate known, and is, therefore, the form in which sulphuric acid is precipitated and weighed in quantitative determinations of this acid. It is also the most insoluble salt of barium, and the form in which barium is determined quantitatively.

Barium sulphate is used as a white pigment, under the name of *permanent white.*

One decomposition of barium sulphate is of more than ordinary interest. *When the sulphate is boiled with a solution of sodium carbonate, it is transformed in part into barium carbonate:* —

$$BaSO_4 + Na_2CO_3 = Na_2SO_4 + BaCO_3.$$

This transformation is at first only partial. If the solution of sodium carbonate and sodium sulphate is poured off after a time, and a new solution of sodium carbonate added, the decomposition of the barium sulphate into carbonate will proceed farther. By repeating this for a few times, practically all of the barium sulphate can be transformed into carbonate. This is one of the very best examples of the effect of mass on chemical activity. By renewing the solution of sodium carbonate, *i.e.* by increasing its mass, and by pouring off the solution of sodium sulphate formed, *i.e.* by decreasing its mass, the transformation in the sense of the above equation can be made practically complete.

Barium Carbonate, $BaCO_3$. — The carbonate of barium, or *witherite,* is the most convenient starting-point in the preparation of compounds of barium. It is easily formed by bringing together a solution of a soluble carbonate with a soluble barium salt: —

$$Na_2CO_3 + BaCl_2 = 2\,NaCl + BaCO_3.$$

We have seen that strontium carbonate is far more difficult to decompose into the oxide and carbon dioxide than calcium carbonate. Barium carbonate is still more difficult to decompose than strontium

carbonate, giving off only a little carbon dioxide when heated to a white heat.

Phosphates of Barium. — The barium ion, $\overset{++}{Ba}$, combines readily with the ions of phosphoric acid, forming insoluble compounds. The *normal phosphate* is formed by the union of the barium ion, $\overset{++}{Ba}$, and the phosphoric acid ion, $\overset{\equiv}{PO_4}$, and has the composition $Ba_3(PO_4)_2$. The *secondary phosphate* is formed when the barium ion, $\overset{++}{Ba}$, and the secondary phosphoric ion, $H\overset{=}{PO_4}$, unite. It has the composition $BaHPO_4$.

Other Insoluble Compounds of Barium. — The barium ion combines with the oxalic ion, $\overset{=}{C_2O_4}$, forming insoluble barium oxalate, BaC_2O_4. It also combines with the chromic ion, $\overset{=}{CrO_4}$, forming insoluble barium chromate, $BaCrO_4$, and with the hydrofluosilicic ion, $\overset{=}{SiF_6}$, forming insoluble barium fluosilicate, $BaSiF_6$.

Detection of Barium. — Barium is easily detected by its characteristic green flame. This flame persists for a long time when a barium salt is held in a Bunsen burner. When examined spectroscopically, a bright green line appears, of a definite wave-length, and this is characteristic of barium. The barium line has a slightly shorter wave-length than the corresponding calcium line.

Relations between Calcium, Strontium, and Barium. — The three alkaline earth metals resemble one another closely in their chemical properties. Certain differences, however, manifest themselves. The different solubilities of the salts of these elements with a given acid are very important, especially in connection with the separation of these elements from one another.

Take the hydroxides of the three elements: Calcium hydroxide is the least soluble; strontium hydroxide is more soluble than calcium; while barium hydroxide is still more soluble than strontium hydroxide.

When we turn to the sulphates we find exactly the opposite relations. Barium sulphate is the most insoluble of the three; then comes strontium sulphate, and finally calcium sulphate.

All three of these elements form insoluble carbonates, while barium alone forms an insoluble chromate.

These differences in solubility are made use of to detect the alkaline earths when in solution in the presence of one another.

Detection of the Alkaline Earths — Calcium, Strontium, and Barium. — Given a solution containing calcium, strontium, and barium ions, how would these be detected in the presence of one another? As we have seen, all of these ions form insoluble com-

pounds with the ion of carbonic acid. Therefore, if ammonium carbonate is added to a solution containing these substances, calcium, strontium, and barium carbonates are precipitated.

The three carbonates are filtered off, washed, and dissolved in a little dilute nitric acid. The solution is evaporated to dryness, and the residue heated until all traces of nitric acid have disappeared. The residue is then treated with a mixture of equal parts of absolute alcohol and ether. Calcium nitrate dissolves, while strontium and barium nitrates remain undissolved. The solution is then filtered off from the residue and treated with a few drops of dilute sulphuric acid, when calcium sulphate is precipitated.

The residue is washed carefully with the mixture of alcohol and ether to remove every trace of calcium, and then dissolved in a little water. A part of the solution is then treated with a few drops of acetic acid, and a solution of potassium chromate added. Barium is precipitated as the chromate.

To the solution from which all the barium has been precipitated as the chromate, add ammonium carbonate and ammonia, when the strontium will be thrown down as strontium carbonate.

CHAPTER XXXI

THE MAGNESIUM GROUP

GLUCINUM, MAGNESIUM, ZINC, CADMIUM, MERCURY

GLUCINUM (At. Wt. = 9.1)

The first two members of this group, glucinum and magnesium, correspond rather closely in their properties to the elements of the calcium group. The first of these elements, glucinum or beryllium, is comparatively rare. It occurs chiefly in the mineral *beryl*, which is a silicate of aluminium and beryllium. It has the composition $Al_2(SiO_3)_3 + 3\,GlSiO_3$. It also occurs as *chrysoberyl*, having the composition $GlO.Al_2O_3$.

The element is conveniently prepared by electrolyzing the chloride. It is white, and decomposes water only at an elevated temperature. It decomposes water only slowly under these conditions, and thus differs from the metals of the calcium group.

Glucinum forms with water the hydroxide $Gl(OH)_2$, which has basic properties and, therefore, yields hydroxyl ions. The hydroxide dissociates in the presence of water as follows: —

$$Gl(OH)_2 = \overset{++}{Gl}, \overset{-}{O}H, \overset{-}{O}H.$$

The dissociation of glucinum hydroxide is not as great as that of calcium hydroxide, or, in a word, it is not so strong a base. This is shown by the fact that in the presence of a strong base like sodium hydroxide it acts as an acid, forming salts with the sodium ion. We shall see that this property is manifested repeatedly by succeeding members of this group, and shall discuss it more fully in connection with them.

Glucinum combines with the anions of strong acids, forming salts in which the glucinum ion, $\overset{++}{Gl}$, is bivalent. The chloride of glucinum has the composition $GlCl_2$. The sulphate, $GlSO_4$, crystallizes both with four and with seven molecules of water, forming $GlSO_4.4\,H_2O$, and $GlSO_4.7\,H_2O$. The carbonate of glucinum, $GlCO_3$, is soluble in water.

Glucinum readily combines with silicic acid forming silicates which have value as gems.

MAGNESIUM (At. Wt. = 24.36)

The second member of the series in the order of increasing atomic weights, but the first member in the order of importance, and the one from which the series takes its name, is magnesium. Magnesium occurs in nature in the form of several salts. Magnesium carbonate, *magnesite*, $MgCO_3$, is fairly widely distributed, while the double carbonate of magnesium and calcium, *dolomite*, forms whole mountain ranges. Magnesium also occurs as the sulphate, $MgSO_4 . H_2O$.—*kieserite.* It occurs in large quantities in *kainite* the double sulphate of magnesium and potassium, which also contains magnesium chloride — $MgSO_4 . K_2SO_4 . MgCl_2 . 6\,H_2O$. *Carnallite* — the double chloride of magnesium and potassium — $MgKCl_3 . 6\,H_2O$, is also found in large quantities in certain salt deposits. The silicates of magnesium and other metals constitute some of the best-known minerals, such as *hornblende, serpentine, talc, asbestos*, etc.

Magnesium is prepared by electrolyzing fused, anhydrous, carnallite. It is a white, ductile metal, which can be readily drawn into wire. In contact with the air at ordinary temperatures it combines with oxygen very slowly. When heated it takes fire and burns with a brilliant white light, which on account of its richness in light of short wave-length is frequently used for illuminating purposes in photography. Magnesium, on account of its power to combine with oxygen at elevated temperatures, is an excellent reducing agent, and is frequently used, as we have seen, to remove oxygen from the oxides of other elements.

Magnesium decomposes water very slowly, indeed, at ordinary temperatures, but quite rapidly when the water is hot. It thus differs from the elements of the calcium group, and resembles more closely the later members of this series. Magnesium combines readily with the halogens.

Magnesium Oxide, MgO, and Magnesium Hydroxide, $Mg(OH)_2$. — Magnesium oxide, or *magnesia*, is formed when magnesium is burned in the air, or when the carbonate or hydroxide of magnesium is heated. Magnesia melts only at enormously high temperatures. It is, therefore, used to line vessels which are subjected to high temperatures.

Magnesium oxide dissolves in water to only a slight extent, forming, however, magnesium hydroxide. Magnesium hydroxide, $Mg(OH)_2$, is not very soluble in water, and is precipitated from

a solution of a magnesium salt by treating this with a soluble hydroxide: —

$$MgCl_2 + 2\,NaOH = 2\,NaCl + Mg(OH)_2.$$

Magnesium hydroxide dissolves readily in ammonium salts, and this is of importance in the detection of magnesium.

Magnesium Chloride, $MgCl_2 . 6\,H_2O$. — Magnesium chloride, like the chlorides of calcium and strontium, contains six molecules of water of crystallization. It occurs in nature in combination with potassium chloride as *carnallite*, and can readily be prepared by dissolving magnesium carbonate or oxide in hydrochloric acid. When heated it does not give up its water of crystallization, leaving the anhydrous salt behind, but undergoes decomposition, giving off hydrochloric acid. The decomposition may be represented thus: —

$$MgCl_2 + H_2O = 2\,HCl + MgO.$$

This reaction is now of importance for obtaining hydrochloric acid on a commercial scale.

Magnesium Sulphate, $MgSO_4 . 7\,H_2O$. — Magnesium sulphate containing one molecule of water occurs in nature, as we have seen, as the mineral *kieserite*, $MgSO_4 . H_2O$. The ordinary salt, known as *Epsom salt* since it is contained in the Epsom springs, contains seven molecules of water, $MgSO_4 . 7\,H_2O$. Magnesium sulphate when heated loses six molecules of water at 150°. The last molecule is retained until a temperature of about 200° is reached. We shall find other examples of this same behavior — salts containing water of crystallization retaining the last molecule to a much higher temperature than the other molecules. Magnesium sulphate is used in medicine as a purgative.

Magnesium sulphate has the power to combine with alkaline sulphates and form double sulphates. An example of this class of substances is the mineral *schönite*, which has the composition $MgSO_4 . K_2SO_4 . 6\,H_2O$. This contains one molecule of magnesium sulphate and one molecule of potassium sulphate. Another double sulphate of magnesium and potassium is the mineral *langbeinite*, $K_2SO_4 . 2\,MgSO_4$, containing two molecules of magnesium sulphate to one of potassium sulphate.

Magnesium Carbonate, $MgCO_3$. — As already stated, magnesium hydroxide is a weak base and carbon dioxide a weak acid. When the two are brought together they form a salt, but there is a strong tendency to form a basic salt. When a soluble carbonate is brought together with a soluble magnesium salt, the normal carbonate of

magnesium is not formed, but carbon dioxide escapes, and there results a basic carbonate, whose composition depends upon the dilution and temperature of the solutions. The greater the dilution of the solutions, and the higher the temperature when they are mixed, the more basic the carbonate which is precipitated. The carbonate formed by adding to a solution of magnesium sulphate a solution of an alkali carbonate has approximately the composition

$$Mg_3(OH)_2(CO_3)_2 = 2\,MgCO_3 + Mg(OH)_2.$$

This is known as *magnesia alba.*

When carbon dioxide is passed into water containing magnesia alba in suspension, the normal carbonate of magnesium, $MgCO_3.3\,H_2O$, crystallizes out of the solution.

Magnesium carbonate, like magnesium sulphate, forms double salts. The best known of these double carbonates is that formed with calcium carbonate. As already mentioned, magnesium carbonate and calcium carbonate crystallize together as *dolomite.* This has the composition $MgCO_3.CaCO_3$, and occurs in great abundance in nature. These two carbonates can apparently crystallize together in all proportions, since many such mixtures are known having very different proportions of the two substances present in them.

Phosphates of Magnesium. — Magnesium forms the primary, $Mg(H_2PO_4)_2$; the secondary, $MgHPO_4$; and the tertiary, or normal, phosphate, $Mg_3(PO_4)_2$. These resemble the phosphates of calcium so closely that a detailed discussion is unnecessary. One phosphate of magnesium, however, is of special interest. This is the ammonium magnesium phosphate already mentioned—$NH_4MgPO_4.6\,H_2O$. This compound is of special importance, since it is the form in which phosphoric acid is precipitated in quantitative determinations of this acid. It is also the form in which magnesium is precipitated in quantitative determinations of magnesium. When heated it decomposes as follows: —

$$2\,NH_4MgPO_4 = 2\,NH_3 + H_2O + Mg_2P_2O_7,$$

yielding magnesium pyrophosphate, which is a very stable substance and of constant composition. It is, therefore, an excellent form in which to weigh either phosphoric acid or magnesium.

Silicates of Magnesium. — Magnesium combines with silicic acid or the polysilicic acids, forming some of the best-known minerals. Ordinary *talc* is a silicate of magnesium having the composition $Mg_3H_2Si_4O_{12}$. *Serpentine* is a silicate of magnesium having the composi-

tion $Mg_3Si_2O_7 . 2\ H_2O$. *Olivine* is the normal silicate of magnesium, Mg_2SiO_4. *Soapstone* is a more complex silicate.

Magnesium silicate combines with other silicates, forming such well-known minerals as *hornblende, tourmaline*, etc.

Magnesium Nitride, Mg_3N_2, is formed by the direct action of nitrogen on red-hot magnesium. Magnesium nitride decomposes with water in the sense of the following equation: —

$$Mg_3N_2 + 6\ H_2O = 2\ NH_3 + 3\ Mg(OH)_2.$$

Separation of Magnesium from the Elements of the Calcium Group. — In an ordinary qualitative analysis magnesium would be precipitated as the basic carbonate along with the carbonates of calcium, strontium, and barium. To prevent this, ammonium chloride is added to the solution until on addition of ammonia no precipitate is formed. The calcium, strontium, and barium are then thrown down by adding ammonium carbonate, as the corresponding carbonates. These are filtered off, leaving the magnesium in the filtrate.

To the solution containing the magnesium, a solution of disodium phosphate is added. The magnesium is precipitated as a secondary phosphate when no ammonia is present, but since some ammonia is added, as magnesium ammonium phosphate.

Magnesium does not give any characteristic flame reaction and cannot, therefore, be detected by this means.

ZINC (At. Wt. = 65.4)

An element closely allied to magnesium in many of its properties, but differing from it markedly in others, is zinc. This well-known element occurs in nature in abundance in a number of compounds. *Zinc blende*, which is the sulphide ZnS, is one of the most common. It also occurs as the carbonate $ZnCO_3$ *smithsonite*, the silicate $Zn_2SiO_4 . H_2O$ *calamine*, and in combination with iron oxide as *franklinite*.

Zinc is prepared by reducing with carbon the oxide, which is usually obtained by roasting the sulphide in the air: —

$$ZnO + C = CO + Zn.$$

The metal boils at 950°, and is, therefore, easily distilled off when once set free. It condenses in the form of a fine powder or dust, which is known as *zinc dust*. The metal can be melted and cast into sticks, or poured into water while molten, and produces *granulated zinc*.

Zinc manifests remarkable behavior on warming. At ordinary temperatures it is brittle. When heated above 100° it becomes malleable, and can be rolled into sheets, drawn into wire, etc. Having once acquired this property, it retains it even at ordinary temperatures. When heated still higher, — to somewhat above 200°, — it

becomes brittle again, and can be readily pulverized. Having become brittle again, it retains this property when the temperature is reduced to the ordinary. Zinc melts at 420°, and combines with oxygen when heated to a much higher temperature, forming zinc oxide. Zinc decomposes water very slowly at ordinary temperatures, but more rapidly at elevated temperatures. The vapor-density shows that the molecule in the form of vapor contains one atom. Zinc is dissolved by hydrochloric and nitric acids. In the former case, hydrogen is evolved; in the latter it acts upon more nitric acid, reducing it, liberating oxides of nitrogen. In sulphuric acid pure zinc dissolves very slowly, if at all. If the zinc is impure, however, it dissolves readily in sulphuric acid with evolution of hydrogen gas. If a piece of platinum wire is wrapped around pure zinc and the whole plunged into sulphuric acid, the zinc dissolves rapidly, and hydrogen is evolved on the platinum. If a little platinic chloride is added to the solution of the acid around the zinc, the same result is produced. This is due to electrical action, the hydrogen from the acid separating more easily upon the impurity, or upon the platinum, than upon the zinc. Zinc is used for covering objects which, if exposed to air or water, would rust. Iron objects thus protected are known as *galvanized.* Iron objects are galvanized by dipping them into molten zinc. Zinc is also extensively used in constructing primary cells. The chief uses of zinc, however, are in alloys with other metals. The best known of these is *brass*, an alloy with copper. When nickel is added, we have the alloy of zinc, copper, and nickel, known as *German silver.* Zinc readily combines with mercury when the clean surface of the metal is brought in contact with the mercury, forming *zinc amalgam.*

Zinc Oxide, ZnO, and Hydroxide, Zn(OH)$_2$. — Zinc oxide is formed when zinc burns in the air. It is known from its general appearance as *philosopher's wool.* It is prepared more conveniently by heating basic zinc carbonate. This loses carbon dioxide and water, and zinc oxide remains behind. Zinc oxide is used as a pigment under the name of *zinc white.* Zinc oxide is almost insoluble in water, so that zinc hydroxide is not prepared by treating the oxide with water.

Zinc hydroxide, $Zn(OH)_2$, is formed when a soluble zinc salt is treated with a small amount of an alkaline hydroxide: —

$$ZnCl_2 + 2\,KOH = 2\,KCl + Zn(OH)_2.$$

Zinc hydroxide is a white, flocculent precipitate, which dissolves readily in acids, forming the corresponding salts. It is therefore

basic with respect to acids, and as it dissolves, must dissociate into zinc and hydroxyl ions, thus:—

$$Zn(OH)_2 = \overset{++}{Zn}, \overset{-}{O}H, \overset{-}{O}H. \qquad (1)$$

Zinc hydroxide also dissolves in strong alkalies, forming salts with these, in which the hydroxide plays the rôle of an acid. If zinc hydroxide is treated with potassium hydroxide in excess, the white precipitate dissolves, forming potassium zincate:—

$$Zn(OH)_2 + 2\,KOH = K_2ZnO_2 + 2\,H_2O.$$

The zinc hydroxide, in the presence of a strong base, acts then as an acid, and must dissociate so as to yield hydrogen ions:—

$$Zn(OH)_2 = \overset{+}{H}, \overset{+}{H}, Z\overset{=}{n}O_2. \qquad (2)$$

The kinds of ions into which certain compounds dissociate is conditioned, then, by the nature of the substance into whose presence they are brought. Thus, zinc hydroxide in the presence of hydrogen ions, dissociates in the sense of equation (1); in the presence of hydroxyl ions, in the sense of equation (2).

Zinc Chloride, $ZnCl_2.H_2O$.—The chloride of zinc is readily formed by dissolving zinc in hydrochloric acid and evaporating the solution to crystallization. When the salt is heated to remove the water it loses hydrochloric acid, and a basic chloride remains behind:—

$$ZnCl_2 + H_2O = HCl + Zn(OH)Cl.$$

To obtain pure anhydrous zinc chloride, the salt with water of crystallization must be heated in an atmosphere of dry, hydrochloric acid gas.

Zinc chloride combines readily with water, and is, consequently, a "mild, dehydrating agent." Like the *bromide* and *iodide* of zinc, it is readily soluble in water, and is dissociated much less than the chlorides of the alkalies or alkaline earths.

Zinc Sulphide, ZnS.—The sulphide of zinc has been referred to as occurring in nature as zinc blende, and as being one of the most important ores of zinc. It is formed as a white precipitate whenever hydrogen sulphide is conducted into a dilute solution of a soluble zinc salt:—

$$ZnCl_2 + H_2S = 2\,HCl + ZnS.$$

The sulphide of zinc is soluble to some extent in strong acids, *i.e.* in the presence of hydrogen ions. In a reaction like the above where a strong acid is liberated, the precipitation of zinc sulphide is

not complete, unless the solution is very dilute, since a portion of it is dissolved in the hydrochloric acid formed as the result of the reaction. If sodium acetate is added to the solution, the hydrochloric acid may be regarded as reacting with this salt, forming sodium chloride which remains dissociated into its ions, and acetic acid:—

$$\overset{+}{H}, \overset{-}{Cl} + \overset{+}{Na}, CH_3\overset{-}{C}OO = \overset{+}{Na}, \overset{-}{Cl} + CH_3COOH.$$

Acetic acid is a very weak acid, which is the same as to say that it is very little dissociated. The hydrogen ions combine with the acetic acid anions, forming the molecule of the acid, and thus we remove the hydrogen ions from the solution and prevent them from dissolving the zinc sulphide.

If the solution of the zinc salt is treated with a solution of an alkaline sulphide, the zinc is completely precipitated, since no free acid is formed as the result of the reaction.

$$ZnCl_2 + K_2S = 2\,KCl + ZnS.$$

Zinc Sulphate, $ZnSO_4 . 7\,H_2O$.—The sulphate of zinc is obtained when a bar of pure zinc is wrapped with a piece of platinum wire, dissolved in pure sulphuric acid, and the solution evaporated to crystallization. The salt is formed on a large scale by heating the sulphide in the presence of oxygen:—

$$ZnS + 2\,O_2 = ZnSO_4.$$

Like other sulphates containing a large number of molecules of water of crystallization, it retains one molecule to a much higher temperature than the remainder. When zinc sulphate is heated slightly above 100° it loses six molecules of water. The last molecule is retained until a considerable higher temperature is reached. On account of its color and composition the salt is known as *white vitriol.*

Zinc Carbonate, $ZnCO_3$, is an important ore of zinc. When heated it decomposes into the oxide and carbon dioxide:—

$$ZnCO_3 = ZnO + CO_2.$$

Zinc carbonate is formed when a soluble zinc salt is treated with a solution of an alkaline carbonate. The precipitate formed under these conditions is not the normal carbonate of zinc, but a basic carbonate containing more or less hydroxyl groups, depending upon the conditions under which it is precipitated.

This compound is of importance in connection with the quantitative determination of zinc. The zinc is precipitated as the basic

carbonate by means of potassium or sodium carbonate, the precipitate filtered off, washed, and ignited. It decomposes into the oxide on heating, and is weighed in this form.

USES OF ZINC IN PRIMARY BATTERIES

Zinc is used more frequently in constructing primary cells than any other known element. This is due to the fact that of all the very common metals zinc has the greatest power to send ions into solution. Whenever a metal is immersed in water or in a solution of one of its salts, it exerts a tension or pressure which tends to drive ions off from the metal into the solution. This is known as the *solution-tension* of the metal. That this tension exists has been demonstrated beyond question in the case of mercury — the only metal liquid at ordinary temperatures.

Demonstration of the Solution-tension of Metals. — A demonstration of the solution-tension of metals has been furnished by Palmaer. Mercury is a metal whose solution-tension is very small. Even when in contact with a very dilute solution of a mercury salt, the solution-tension of the mercury is less than the osmotic pressure of the mercury ions in the solution; and some of the mercury ions will separate from such a solution.

Given a vessel whose bottom is covered with metallic mercury, and over this is placed a solution of mercurous nitrate having a volume of 2000. A few mercury ions will separate from the solution and give up their positive charges to the mercury. The positively charged mercury will attract electrostatically a few negative nitric ions, $\overline{N}O_3$, to form the double layer. This will be continued until a certain difference in potential has been reached, when equilibrium will be established. If a drop of mercury is now let fall into the solution, a few mercury ions will separate upon it, charge it positively, and it will then attract an equal number of negative nitric ions, $\overline{N}O_3$, and drag them down with it through the solution. The next drop of mercury will behave in exactly the same manner, and thus the top of the solution will become continually poorer and poorer in the salt.

When the drop of mercury comes in contact with the mercury at the bottom of the vessel where equilibrium is already established, what will happen? When the drop has united with the mercury, this will contain an excess of positive electricity, and, therefore, a small quantity of mercury ions will pass into solution. And, indeed, exactly the same number as there are nitric ions, NO_3, brought down

from the top to the bottom of the solution. The solution will thus become more concentrated just above the layer of mercury on the bottom of the vessel.

A fine glass tube from which mercury flows is known as a drop-electrode. To produce changes in concentration sufficient for the purposes of a demonstration, a very powerful drop-electrode must be used. This is made by inserting a conical glass stopper into a conical glass tube, so that the junction is mercury-tight. A large number of fine grooves are then etched on the outside of the stopper, so that the mercury will stream through as a fine mist. To assist this process the mercury is subjected to four or five atmospheres of pressure.

Under these conditions, however, the mercury cannot be allowed to flow directly into a vessel filled with a dilute solution of a mercury salt, and containing mercury at the bottom, since there would be too much commotion in the solution. The arrangement which was used is shown in Fig. 37. The drop-electrode *T* dips into the funnel-shaped vessel *O*, which is connected by a narrow tube and a rubber tube with the larger vessel *M*. This is in turn connected with the vessel *U*, where the change in concentration can be observed. When the mercury has been allowed to flow for five minutes under a pressure of five atmospheres, distinct changes in concentration can be detected.

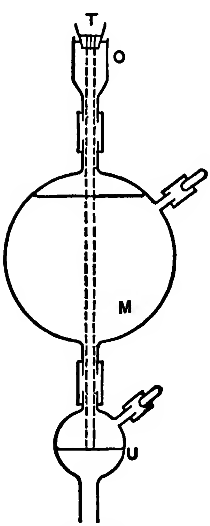


FIG. 37.

Palmaer gives data which show that the concentration above had been diminished as much as fifty per cent, and increased below as much as forty per cent.

This will be recognized at once to be a very remarkable experiment, and before our modern physical chemical theories were proposed would have been entirely inexplicable. The results of this experiment were predicted before the experiment was tried.

The Relative Solution-tensions of Some of the More Common Metals. — It would lead us much too far to discuss here the method of determining the relative solution-tensions of metals. To study the principle and method some work on physical chemistry must be consulted. A few of the results obtained are the following: —

Metal	Solution-tension in Atmospheres
Magnesium	10^{44}
Zinc	10^{18}
Aluminium	10^{18}
Cadmium	3×10^{6}
Iron	10^{4}
Cobalt	2×10^{0}
Nickel	1×10^{0}
Lead	10^{-3}
Mercury	10^{-16}
Silver	10^{-17}
Copper	10^{-20}

Magnesium and aluminium as well as zinc have high solution-tensions, or a great power to send off ions into solution, but these are far less abundant and more expensive substances than metallic zinc.

Solution-tension of Metals and Primary Cells. — The question which arises is, What has the solution-tension of metals, or their power to throw ions off into the solution, to do with the production of electricity in a primary cell? Why is zinc used in primary cells because it has a high solution-tension, or stands near the top of the *tension-series*, as the above order of the metals is termed?

We have seen that all dissolved substances exert an osmotic pressure. When a bar of zinc is dipped into a solution of a zinc salt, say zinc chloride, the osmotic pressure of the zinc ions in the solution tends to drive these ions out of the solution on to the bar of metal, in the atomic condition. In order that an ion may become an atom it must give up its electrical charge to something, and in this case the only thing to which it can give it up is the bar of zinc.

The solution-tension of the metal exerts exactly the opposite influence. It tends to drive atoms of metal off from the bar into the solution as ions. What will happen when a bar of metal is immersed in a solution of one of its salts, depends upon which of these forces is the greater. Let us call the solution-tension of the metal P, and the osmotic pressure of the cations in the solution p. If $P > p$ the metal will send ions into the solution, and in doing so will become *negatively charged*, since it gives up electricity to convert atoms into ions. If, on the other hand, $P < p$ ions will separate out of the solution on to the bar as atoms, and in doing so will give up their charge

to the bar, which will become *positively charged.* If $P = p$ nothing will happen when the metal is immersed in the solution of its salt.

The object, then, in using a metal with a high solution-tension on one side of the cell is to have this electrode charged negatively with respect to the surrounding solution.

With these conceptions of the relation between osmotic pressure and solution-tension of the metals we can easily understand the action of a primary cell.

Concentration Element. — The simplest form of primary cell in which zinc is employed is the following: A bar of zinc, B (Fig. 38), is immersed in a solution of zinc chloride of a definite concentration, say one-tenth normal. At any concentration of solution of a zinc salt $P > p$, since P is so very great. The bar of zinc will send ions

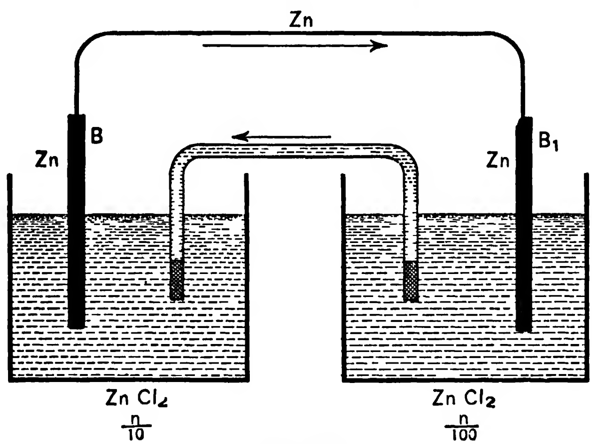


FIG. 38.

into the solution until a definite difference in potential is established between the metal and the solution, the zinc being negative.

On the other side of the cell a bar of zinc, B_1, is immersed in a solution of zinc chloride of a different concentration, say one-hundredth normal. Here the zinc will throw ions into the solution and will do so to a greater extent than the other bar, since the osmotic pressure of the zinc ions in the solution, which is the counter force, is less. The bar will become negative with respect to the solution, and still more negative than the first bar. Let the two sides of the cell be connected. A current will flow from the bar B to the bar B_1, since the latter is negative with respect to the former. Zinc ions will continue to separate on B from the solution of the zinc salt around it, and to dissolve from B_1 as the current flows; the chlorine

anions moving against the current in the solution from B to B_1. This cell is called a concentration element, since its whole action depends on the difference in the concentration of the two solutions of the same electrolyte which are used. During the flow of the current the more concentrated solution becomes more dilute and the more dilute solution more concentrated, and the cell will cease to be active when the two concentrations have become equal.

The electromotive force of such an element is calculated from an equation derived very easily from the fundamental equation: —

$$^{1}\ \pi = 0.058 \log \frac{p_1}{p_2}.$$

p_1 is the osmotic pressure of the zinc ions in the more concentrated solution of zinc chloride, and p_2 the osmotic pressure of the zinc ions in the more dilute solution of zinc chloride.

If the action of this, the simplest form of primary cell, is understood, we are in a position to understand easily the action of any form of primary battery.

The Daniell Cell. — We shall discuss briefly one very common form of cell in which zinc is used as one electrode — the Daniell cell. This is sketched diagrammatically in Fig. 39. It consists of a bar of zinc immersed in a solution of zinc sulphate on one side, and a bar of copper surrounded by a solution of copper sulphate on the other. While zinc is a metal with very high solution-tension, copper has a very small solution-tension. A bar of zinc immersed in any solution of a zinc salt will send ions into solution and become negatively charged. A bar of copper immersed in almost any solution of a copper salt will receive ions from the solution and become positively charged. When the two electrodes are connected, and the two electrolytes connected by a siphon filled either with the zinc sulphate or the copper sulphate, we have a Daniell cell.

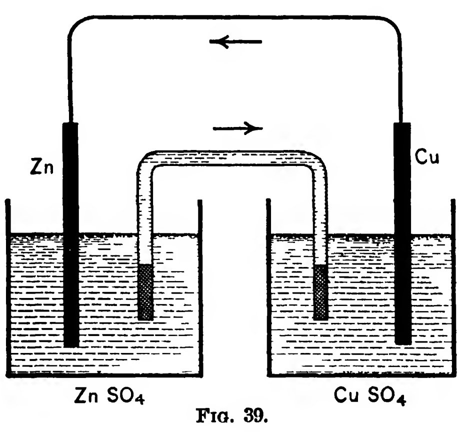


FIG. 39.

[1] It would lead too far to derive even this equation here. Consult some work on physical chemistry.

The zinc passes into solution, and the copper separates from the solution. The zinc is, therefore, negative and the copper positive, and the current flows in the direction shown by the arrows. Copper is used because it has a very low solution-tension and occurs in abundance.

The electromotive force of this element is calculated by means of the equation —

$$\pi = .029 \log \frac{P}{p} - .029 \log \frac{P_1}{p_1}$$

in which p and p_1 are the osmotic pressures of the zinc and copper ions respectively, and P and P_1 the solution-tensions of zinc and copper. The solution-tensions of the two metals come into play in the calculation of the electromotive force of the Daniell cell, since they have different values. In the calculation of the electromotive force of the concentration element, the solution-tension of the zinc is the same on both sides of the cell, and, consequently, enters the equation twice, but with equal value and opposite sign. It, therefore, entirely disappears from the equation.

To show that zinc is used in almost all of the best-known forms of primary cells it is only necessary to mention the Grove, Leclanché, and bichromate cells.

CADMIUM (At. Wt. = 112.4)

A comparatively rare element which is closely allied in its properties to zinc is cadmium. It usually occurs associated with zinc ores, either in the form of the oxide or sulphide. The oxide of cadmium, like that of zinc, is easily reduced by heated carbon: —

$$CdO + C = CO + Cd.$$

The metal boils at 778° and, therefore, distils over before the zinc.

The vapor-density of cadmium shows that *the molecule consists of one atom*. There are a few cases where the molecule of an element is monatomic, but very few, and most of them are in this group of elements.

Cadmium unites with oxygen at an elevated temperature, forming cadmium oxide CdO. This is a brown powder, as obtained by direct combination of the elements, and also by decomposing the carbonate by heat. When the nitrate is heated the residue is cadmium oxide, but this is very dark brown, or brownish-black. *Cadmium hydroxide* is formed when a soluble salt of cadmium is treated with an alkaline hydroxide: —

$$Cd(NO_3)_2 + 2\,NaOH = 2\,NaNO_3 + Cd(OH)_2.$$

Cadmium hydroxide is not soluble in an excess of the alkaline hydroxide, showing that the acid properties which are manifested by zinc hydroxide are lost in cadmium with the higher atomic weight. While cadmium under ordinary conditions forms only the ion $\overset{++}{Cd}$, yet it is capable of forming compounds in which it acts as a univalent ion. The *suboxide of cadmium*, Cd_2O, has been prepared. Also the subhydroxide, CdOH.

Salts of Cadmium. — The cadmium ion $\overset{++}{Cd}$ unites with the anions of acids, forming salts which closely resemble the corresponding compounds of zinc.

The *chloride*, $CdCl_2$, $2\,H_2O$, is readily formed by the action of hydrochloric acid on the metal or on the carbonate. Its chief interest from a physical chemical standpoint is in connection with its dissociation. While the halides of zinc are less dissociated than those of the alkalies and alkaline earths, the halides of cadmium are much less dissociated than those of zinc. Of these, cadmium bromide is dissociated less than the chloride, and the iodide less than the bromide.

Cadmium chloride, like the chloride of zinc, combines with the chlorides of the alkalies and alkaline earths, forming such compounds as the following: —

$$KCl.CdCl_2,\ 2\,KCl.CdCl_2,\ CaCl_2.CdCl_2.KBr.CdBr_2,\ BaBr_2.CdBr_2.$$

These are the so-called *double halides*, of which many hundred examples are known.

Cadmium sulphide, CdS, occurs in nature as *greenockite* and is formed when hydrogen sulphide is passed into a solution of a cadmium salt: —

$$CdCl_2 + H_2S = 2\,HCl + CdS.$$

This is a beautiful, yellow precipitate, and is soluble to some extent in strong acids. Although soluble in strong acids it is much less soluble in acids than zinc sulphide, and is thrown down nearly quantitatively from its neutral salts by hydrogen sulphide. By an alkaline sulphide cadmium is precipitated quantitatively, and this is one of the methods of determining the amount of cadmium present. On account of its fine yellow color it is used as a pigment by artists, under the name of "cadmium."

The *sulphate* containing seven molecules of water, $CdSO_4$, $7\,H_2O$, is known. The sulphate which is ordinarily formed, however, has the composition $3\,CdSO_4$, $8\,H_2O$.

The *carbonate* of cadmium, $CdCO_3$, is formed when soluble cadmium salts are treated with soluble carbonates: —

$$CdCl_2 + Na_2CO_3 = 2\,NaCl + CdCO_3.$$

The compound is of importance because it is the form in which cadmium is frequently precipitated in analysis.

Cadmium belongs to that group of elements whose sulphides are precipitated from their neutral salts by hydrogen sulphide, and whose sulphides are insoluble in ammonium sulphide.

MERCURY (At. Wt. = 200.0)

Mercury occurs in nature in the elementary condition, but much more abundantly in the form of the sulphide, HgS, *cinnabar*. The chief localities are Almaden in Spain, California, and Hungary Mercury is readily obtained by heating the sulphide in contact with the air. The metal distils over and is condensed, and the sulphur is oxidized to sulphur dioxide.

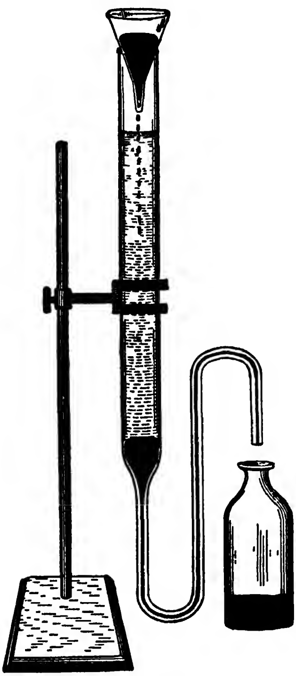


FIG. 40.

Mercury is purified by passing it in fine drops through a solution of ferric chloride, through nitric acid, or by shaking with sulphuric acid containing a little chromic acid. The impurities are oxidized while the mercury is unattacked. The apparatus used to purify mercury is shown in Fig. 40. The mercury flows through the funnel, whose end is fused so nearly together that the drops of mercury which pass through are very fine. The tube contains the purifying liquid. The mercury is collected in the flask.

Properties of Mercury. — Mercury combines with oxygen only at elevated temperatures, but combines with the halogens at ordinary temperatures. Mercury forms a univalent mercurous ion, $\overset{+}{Hg}$, and a bivalent mercuric ion, $\overset{++}{Hg}$. Both of these ions combine with the anions of acids, forming salts. The former are known as "mercurous," the latter as "mercuric" salts.

Mercury is distinguished by the fact that it is the only metal known which is liquid at ordinary temperatures. It solidifies at $-39°.4$. The specific gravity of mercury is 13.595. On account of its low melting-point and its high density it is very valuable in the preparation of barometers, thermometers, and other physical and chemical apparatus. If mercury were not a liquid at ordinary

temperatures the science of chemistry would undergo some fundamental changes.

Mercury has an appreciable vapor-tension at temperatures not very far above the ordinary, and since its vapor is quite poisonous care must be exercised in dealing with it. It boils at 358°, and passes into a vapor whose density is 99.4 in terms of hydrogen as unity. Its molecular weight is, therefore, 198.8, which is identical with the atomic weight. The *atom and molecule of mercury in the form of vapor are identical,* and this is the fourth member of this group where this relation obtains.

Amalgams. — Many of the metals dissolve readily in mercury, forming amalgams, which are really solutions of the metals in mercury as a solvent. Such metals as magnesium, zinc, cadmium, silver, gold, the alkaline earths, the alkalies, and many others dissolve without serious difficulty in mercury. The amalgams of sodium have already been referred to. The one containing one per cent of sodium is a liquid, while double the amount of sodium gives a solid solution in mercury. Such compounds as Hg_6Na and $HgNa_3$ have been obtained.

The ammonium amalgam formed by bringing ammonium chloride in contact with sodium amalgam has also been referred to (p. 207). These amalgams are often useful in electrochemical investigations, where it is found to be more convenient to use the amalgam than the pure metal.

Molecular Weights of Metals in Mercury. — The question naturally arises, What is the molecular weight of the metal in question dissolved in mercury? There are two methods available for throwing light on this question; the freezing-point, and the boiling-point or the vapor-tension method. The lowering of the vapor-tension is proportional to the rise in boiling-point, and the one phenomenon can be used as well as the other for determining molecular weights.

The results obtained for the molecular weights of a few metals in mercury, as determined by the lowering of the freezing-point of the mercury, are as follows: —

	Mol. Wt.	At. Wt.
Potassium	26–55	39
Sodium	21–25	23
Thallium	141–221	200
Zinc	51–66	65

The mean of the values found experimentally shows that for these four elements the molecular weights in mercury are the same as the atomic weights, or the molecules are monatomic.

The results found by the lowering of the vapor-tension of mercury are even more interesting. A few are given below: —

	Mol. Wt.	At. Wt.
Lithium	7.10	7.02
Calcium	19.1	40.1
Barium	75.7	137.0
Magnesium	24–21.5	24.3
Manganese	55.5	55.0

In these and in all other cases investigated the molecular weight was never greater than the atomic weight. In some cases, as with calcium and barium, the molecular weight is about one-half of the atomic weight. There is other evidence that the supposed atom of calcium can be broken down into two or more parts. This evidence is based on the shift in the position in the spectrum of the calcium lines under pressure, but cannot be discussed here.

Mercurous (Hg_2O) and Mercuric (HgO) Oxides. — Mercurous oxide is formed when a mercurous salt is treated with an alkali: —

$$2\,HgCl + 2\,NaOH = 2\,NaCl + H_2O + Hg_2O.$$

By light, heat, or friction, it is decomposed into mercury and oxygen. It is a black powder and obviously unstable.

Mercuric oxide is formed when mercury is heated for a long time in the air. It is also obtained as a *red* powder by heating the nitrate.

It is also formed by treating a mercuric salt with sodium hydroxide: —

$$HgCl_2 + 2\,NaOH = 2\,NaCl + H_2O + HgO.$$

Prepared in this way it is *yellow*, but becomes red on gentle heating. The difference in color in this case seems to be purely mechanical, depending on the size of the particles.

Mercurous ($HgCl$) and Mercuric ($HgCl_2$) Chlorides. — Mercurous chloride is the familiar substance *calomel*. It is formed by heating a mercurous salt with a soluble chloride: —

$$Hg_2SO_4 + 2\,NaCl = Na_2SO_4 + 2\,HgCl.$$

Calomel is also formed by subliming a mixture of mercury and mercuric chloride: —

$$HgCl_2 + Hg = 2\,HgCl.$$

It is also formed by reducing mercuric chloride with such a reducing agent as sulphur dioxide: —

$$2\,HgCl_2 + 2\,H_2O + SO_2 = H_2SO_4 + 2\,HCl + 2\,HgCl.$$

Mercurous chloride is a white powder which can easily be obtained in crystals by sublimation. It is difficultly soluble in water, and is therefore taken into the system slowly when used as a medicine.

Mercurous chloride is readily oxidized to the mercuric salt, which is quite poisonous. This oxidation is effected by nitric acid, and the same transformation is effected by hydrochloric acid and the alkaline chlorides. Mercurous chloride is partly transformed into mercuric chloride by the action of light. When calomel is exposed for a considerable time to the action of light it contains the very poisonous substance, mercuric chloride, and should never be used as a medicine. Calomel, which is to be used for such purposes, should always be carefully protected from all agents which transform it into mercuric chloride. The vapor-density shows that the molecule of mercurous chloride is HgCl and not Hg_2Cl_2. Mercuric chloride, or *corrosive sublimate*, is formed by subliming a mixture of sodium chloride and mercuric sulphate. The following reaction takes place: —

$$2\,NaCl + HgSO_4 = Na_2SO_4 + HgCl_2.$$

Mercuric chloride is a white, crystalline compound, readily soluble in water, and still more easily soluble in a mixture of alcohol and ether. It boils at 307°, and its vapor-density shows that it has the formula $HgCl_2$. On account of its solubility it furnishes a convenient means of obtaining mercuric ions, $\overset{++}{Hg}$, which are very poisonous to most forms of life. Mercuric chloride is, therefore, an excellent disinfectant, and is extensively used in surgery for this purpose.

Mercuric chloride, like the salts of mercury in general, is only slightly dissociated into ions. We saw that the compounds of zinc with the halogens are far less dissociated than the corresponding compounds of the alkalies and alkaline earths. Passing to the next member of this series in the order of increasing atomic weights, cadmium, we saw that its halogen compounds were dissociated less than those of zinc. We come now to mercury, the next member of the series, and find that its halides are dissociated relatively very little. The conductivity of mercuric chloride in water is very small indeed. Mercuric chloride has the power to combine with the halides of the alkalies and alkaline earths, forming so-called *double chlorides.* These have the composition $MHgCl_3$ and M_2HgCl_4, where M corresponds to

a univalent alkali metal, and M_1HgCl_4, where M_1 is an alkaline earth metal. These can be regarded as compounds of complex acids of the composition H_2HgCl_3 and H_2HgCl_4 and are definite chemical compounds, as has been shown by the way in which they dissociate in the presence of water. When the double halides of mercury and especially of cadmium are electrolyzed, the mercury or cadmium passes in part to the anode, showing that there exists a complex anion composed of the less alkaline metal and the halogen. This is the anion of the complex halogen acid of which the above compounds are salts.

Mercuric chloride is easily reduced to mercurous chloride, just as the mercurous chloride is easily oxidized to mercuric. The reducing action of sulphur dioxide has already been considered in connection with the preparation of mercurous chloride.

Oxalic acid reduces mercuric chloride in the presence of light, and this reaction has been made use of to measure the intensity of the light, as in photometry: —

$$2\,HgCl_2 + H_2C_2O_4 = 2\,HCl + 2\,CO_2 + 2\,HgCl.$$

Mercuric chloride is also reduced by stannous chloride, first to mercurous chloride: —

$$2\,HgCl_2 + SnCl_2 = SnCl_4 + 2\,HgCl;$$

and if enough stannous chloride is present, to metallic mercury: —

$$HgCl_2 + SnCl_2 = SnCl_4 + Hg.$$

Mercuric Bromide ($HgBr_2$) and Iodide (HgI_2). — The bromide of mercury resembles strongly the chloride. The iodide presents certain features of special interest. It is formed by rubbing together mercury and iodine in the proper proportions; if too much mercury is used the mercurous iodide will be formed. It is prepared most conveniently by adding potassium iodide to a solution of a mercuric salt: —

$$Hg(Cl)_2 + 2\,KI = 2\,KCl + HgI_2.$$

It is easily soluble in alcohol, and crystallizes from the alcoholic solution in beautiful, scarlet-red crystals, which belong to the tetragonal system. When the red modification is heated above 126° it turns yellow, and when more highly heated, melts and forms a yellow liquid, which, at a still higher temperature sublimes and forms yellow crystals belonging to the orthorhombic system. When the yellow modification cools below 126° it passes again into the red. If placed in a position where it is not subjected to mechanical dis-

turbance the yellow form may exist below 126°. We have here an *enantiotropic* substance existing in two forms which are mutually transformable — the transition temperature being 126°.

When mercuric iodide is precipitated at low temperatures the yellow modification is formed. After a time this passes over into the red. When either modification is volatilized the vapors condense as the yellow modification. The action of light is to accelerate the transformation from the yellow to the red modification. Mechanical disturbance causes the yellow form to pass into the red. If a vessel containing the yellow modification is struck a few times, the red modification will begin to appear.

Mercuric iodide dissolves readily in a solution of potassium iodide, forming the double iodide K_2HgI_4: —

$$HgI_2 + 2\,KI = K_2HgI_4.$$

This may be regarded as the potassium salt of the complex acid H_2HgI_4. Solutions of this salt do not show the ordinary reactions of mercury, nor is there any reason for supposing that they would do so. The mercury is combined with four iodine atoms, forming the complex anion $\overset{=}{Hg}I_4$, and in this the mercury is doubtless playing a very different rôle with respect to energy relations than when alone. When caustic potash is added to the solution of potassium mercuric iodide we have *Nessler's reagent,* which is a very sensitive means of testing for ammonia; minute traces of ammonia forming a characteristic, yellowish-brown color in a solution of this reagent. This is due, as we shall see, to the formation of complex compounds of ammonia and mercury, some of which have very characteristic colors.

Mercuric Sulphide, HgS. — Only one compound of mercury with sulphur is known, and this is the one in which the mercury is bivalent. When hydrogen sulphide is brought into the presence of a mercurous salt, a mixture of black mercuric sulphide and mercury is thrown down: —

$$2\,HgCl + H_2S = HgS + Hg + 2\,HCl.$$

When mercury and sulphur are rubbed together the sulphide is formed. It is also formed by passing hydrogen sulphide for a time through a solution of a mercuric salt: —

$$HgCl_2 + H_2S = 2\,HCl + HgS.$$

When hydrogen sulphide is passed through a solution of a mercuric salt at first a white precipitate is formed. This is a

compound of the original mercury salt with mercuric sulphide, such as $HgCl_2.HgS$, $HgCl_2.2\,HgS$, and so on. By continuing to pass in hydrogen sulphide the effect of mass comes into play, and such complex compounds as the above are gradually broken down; all of the mercury being transformed into mercuric sulphide. This is shown by the gradual transformation of the white precipitate into gray, and finally black.

The crystallized form of mercuric sulphide, which occurs in nature as *cinnabar*, is grayish-red in mass, but when powdered is red. On account of its beautiful color the artificial sulphide called *vermilion* is used as a pigment.

The black modification is the unstable form since it is produced first, and because it passes over slowly into the red modification, especially in the presence of alkali sulphides. Further, when the red modification is heated it becomes dark. If not heated to too high a temperature the dark modification becomes red again on cooling.

Mercury sulphide is an important substance, because mercury is usually precipitated in this form in analytical operations. Mercury sulphide does not dissolve in dilute nitric acid. It is thus distinguished from all the sulphides which are precipitated in the presence of dilute acids. These sulphides are warmed with dilute, nitric acid, when all dissolve except the sulphide of mercury.

Mercurous (Hg_2SO_4) and Mercuric ($HgSO_4$) Sulphates. — Mercurous sulphate is formed by the action of hot, concentrated sulphuric acid on mercury: —

$$2\,Hg + H_2SO_4 = Hg_2SO_4 + H_2,$$
$$H_2SO_4 + H_2 = 2\,H_2O + SO_2.$$

Mercurous sulphate is difficultly soluble in water, and is extensively used in preparing standard cells with constant electromotive force. The normal element of *Latimer Clark* consists of mercury covered with a thick paste of mercurous sulphate, which serves as one electrode. Above this a thick paste of zinc sulphate into which a bar of zinc is immersed serves as the other electrode. Such an element has an electromotive force of 1.4328 volts, $-0.0012\,(t - 15°)$, t being the temperature at which the element is used.

Another normal element in which mercurous sulphate is used is the *Weston cadmium* element. This consists of mercury covered with a paste of mercurous sulphate, and over this a paste of cadmium sulphate into which a bar of cadmium dips. The electromotive force of this element is 1.0186 volts, and it has a very small temperature coefficient.

Mercuric sulphate is practically insoluble in water, but is decomposed by it, forming a basic salt. This is a yellow compound having the composition $HgSO_4.2\,HgO$.

Mercuric Cyanide, $Hg(CN)_2$, is formed when Prussian blue is boiled with mercuric oxide. It is also formed when mercuric oxide is dissolved in hydrocyanic acid. When heated it decomposes as follows: —

$$Hg(CN)_2 = Hg + 2\,CN.$$

This, as we have seen, is the most convenient method of preparing cyanogen. Mercuric cyanide combines readily with potassium cyanide, forming the compound $K_2Hg(CN)_4$.

We have seen that the salts of mercury are in general only slightly dissociated. Also that hydrocyanic acid is one of the very weakest acids, and is almost undissociated. We would, therefore, expect that mercuric cyanide would be very slightly dissociated, and such is the fact. *An aqueous solution of pure, mercuric cyanide conducts the current only a little better than pure water.*

This shows that we must not conclude that all salts are dissociated and conduct the current because most of them do so. Here is an excellent example of a salt which shows practically no dissociation. It should, however, be added that there are only a few analogous cases.

The mercury compound of an acid whose composition is the same as that of cyanic acid, HOCN, is explosive. The compound has the composition $HgC_2N_2O_2$, and is known as *fulminating mercury.*

Action of Ammonia on Salts of Mercury. — When ammonia is added to a mercurous salt a black precipitate is formed. When ammonia is allowed to act on mercurous chloride the following reaction takes place: —

$$2\,NH_3 + 2\,HgCl = NH_4Cl + NH_2Hg_2Cl.$$

This is ammonium chloride in which two hydrogen atoms are replaced by a mercury atom, and is known as *mercurous chloramide* — the group NH_2 being known as the amido group. It should be stated that this substance is regarded by some as a mixture of mercury and the compound NH_2HgCl.

When mercurous chloride is treated with gaseous ammonia the following reaction takes place: —

$$HgCl + NH_3 = HgNH_3Cl,$$

which is ammonium chloride, in which one hydrogen atom is replaced by mercurous mercury. This is known as *mercurous ammonium chloride.*

When mercuric chloride is treated with ammonia the following reaction takes place: —

$$2\,NH_3 + HgCl_2 = NH_4Cl + HgNH_2Cl.$$

This is ammonium chloride, in which two hydrogen atoms have been replaced by mercuric mercury. From its properties, its color, and the fact that it sublimes without melting, it is known as *infusible white precipitate.*

If a solution of mercuric chloride is added to a boiling solution of ammonium chloride in which there is some free ammonia, the following reaction takes place: —

$$HgCl_2 + 2\,NH_3 = Hg(NH_3Cl)_2.$$

This consists of two molecules of ammonium chloride, in each of which one atom of hydrogen is replaced by one-half of a mercuric mercury atom. It is, therefore, known as *mercuric diammonium chloride,* or since the salt readily melts, as *fusible white precipitate.*

Variable Valence. — We have studied a number of non-metals which showed different valence under different conditions. This is, however, the first metal which we have encountered in which two different valencies clearly manifest themselves. We have a well-defined mercurous ion $\overset{+}{Hg}$, in which the mercury carries only one electrical charge. This forms, with the anions of acids, a class of salts which have definite properties. From these salts the mercurous mercury is precipitated by bases as the black mercurous oxide. Hydrochloric acid throws down insoluble mercurous chloride. Hydrogen sulphide precipitates a mixture of mercuric sulphide and mercury.

The mercuric ion, $\overset{++}{Hg}$, has its own characteristic properties, forming compounds also with the anions of acids From these compounds it is precipitated by hydrogen sulphide, as mercuric sulphide. The alkaline hydroxides precipitate mercuric oxide, while stannous chloride in excess throws down metallic mercury.

CHAPTER XXXII

THE EARTH METALS

ALUMINIUM AND THE RARE ELEMENTS, — SCANDIUM, GALLIUM, YTTRIUM, INDIUM, LANTHANUM, YTTERBIUM, THALLIUM, SAMARIUM

ALUMINIUM (At. Wt. = 27.1)

Occurrence and Preparation. — Of the elements of this group only one occurs in any abundance, and this is aluminium. The remainder are rare substances and will be considered briefly.

Aluminium is a very important constituent of the crust of the earth (see p. 6). The oxide of aluminium, known as *corundum*, is very abundant, and the precious stones *ruby* and *sapphire* are aluminium oxide colored by a small amount of other substances.

The double silicates of aluminium and the alkalies are among the most common minerals. *Mica* is a double silicate of aluminium and one of the alkalies, having the general composition $MAlSiO_4$, in which M is a univalent alkali. The more common *feldspars* are silicates of aluminium and one of the alkalies, sodium or potassium. They have the general composition $MAlSi_3O_8$. *Bauxite* is a hydroxide of aluminium containing iron. *Kaolin* and *clay* are more or less pure hydrous silicates of aluminium, while *cryolite*, found in Greenland, is a double fluoride of sodium and aluminium, having the composition $3NaF.AlF_3$ This compound is of importance in connection with the preparation of the element

Aluminium, named from alum in which it occurs, was prepared first by the great German chemist, Wöhler, who heated the chloride with metallic sodium.

Aluminium is prepared to-day by the electrolytic method. The compound electrolyzed is aluminium oxide. On account of the high fusing-point of aluminium oxide, a bath of cryolite is used, and into the fused cryolite the aluminium oxide is introduced as desired. The cryolite is fused in iron crucibles, which are sometimes lined with carbon. This serves as the cathode upon which the metal separates; the oxygen set free combines with the anode, which con-

sists of bars of carbon introduced into the fused cryolite. The mass is kept molten by the heat generated by the current. Since the introduction of the electrolytic method of preparing aluminium, this metal has become quite abundant and its price lessened many hundred fold. This method, extensively applied at Pittsburg and elsewhere, is known as the Hall method.

Properties of Aluminium. — Aluminium is a metal with remarkable properties. It is ductile and malleable and can be readily drawn into wire or hammered into thin foil. It is very light for a metal, having a specific gravity of only 2.7. It can, nevertheless, withstand considerable strain, but by no means as great as was supposed before it was prepared on a large scale. Its softness also detracts from its commercial value. It melts at about 700°, and can, therefore, be readily moulded. It is an excellent conductor of both heat energy and electrical energy.

Chemically, aluminium is fairly resistant. In contact with moist air it becomes covered with a very thin layer of oxide, which protects the metal from further action. It does not act appreciably upon water, even at elevated temperatures. It dissolves readily in hydrochloric acid, while nitric and sulphuric acids act only at elevated temperatures. It is readily attacked by alkalies, and this is another defect commercially.

While aluminium does not combine readily with oxygen at ordinary temperatures, it combines with great vigor at high temperatures. At these elevated temperatures it is, therefore, an excellent reducing agent. This reducing action is utilized commercially for preparing certain elements, as well as for producing locally very high temperatures, since an enormous amount of heat is produced when aluminium combines with oxygen. When a mixture of finely divided aluminium and ferric oxide is heated by an ignited magnesium wire, or by a primer consisting of a mixture of finely powdered magnesium and barium dioxide, the mixture becomes intensely hot and the aluminium takes the oxygen from the iron, leaving the latter in the molten condition. The temperature of 3000° can be reached by means of this reaction. This is utilized to heat iron bolts white hot, weld iron rails, and the like. The iron from the reduced oxide remains behind as a fused mass.

By means of this same reaction chromium, manganese, and similar elements can be prepared from their oxides.

The *alloys of aluminium* are frequently of considerable commercial value. The alloy with copper known as *aluminium bronze*, containing 6 to 8 per cent aluminium, is used for constructing certain

forms of scientific apparatus. The alloy containing from 12 to 20 per cent of magnesium is known as *magnalium*. It has a specific gravity of from 2 to 2.5, and from its properties promises to be very useful.

Aluminium Amalgam. — Aluminium does not combine as readily with mercury as many of the metals. If, however, a clean piece of aluminium is introduced into a dilute solution of mercuric chloride, the amalgam quickly forms. The aluminium in the amalgam seems to be very much more active chemically than ordinary aluminium, this "active aluminium" decomposes water vigorously at ordinary temperatures, forming aluminium hydroxide. The aluminium under these conditions is really no more active than ordinary aluminium. The difference is that a clean surface of the metal is exposed to the water. The thin coating of oxide which covers the surface of the metal is removed by the alloy being liquid, and a fresh surface is continually exposed to the action of water or the oxygen of the air.

Aluminium Oxide (Al_2O_3) and Hydroxide ($Al(OH)_3$). — The oxide of aluminium occurs in nature, as has already been mentioned. Its most common form is *corundum*. *Sapphire* is a blue variety used as a gem, while *ruby* is a red sapphire. A violet variety is known as *oriental amethyst*, and a yellow variety as *oriental topaz*.

Aluminium oxide is easily prepared by heating aluminium hydroxide: —

$$2\,Al(OH)_3 = Al_2O_3 + 3\,H_2O.$$

Metallic aluminium is prepared chiefly from the oxide, and especially from the variety containing iron, known as *bauxite*.

Aluminium hydroxide occurs in nature as *hydrargillite*. This substance minus one molecule of water is known as *diaspore*, $HAlO_2$. It is readily prepared by treating a soluble aluminium salt with a base: —

$$AlCl_3 + 3\,NH_4OH = 3\,NH_4Cl + Al(OH)_3.$$

Aluminium hydroxide is very slightly soluble in water, and is a very weak base. It can, however, form three classes of salts in which one, two, and three acid anions, respectively, are present. Thus, we may have $Al(OH)_2A$, $Al(OH)A_2$, and AlA_3, where A is a univalent anion. The first two substances are *basic salts*. Since aluminium hydroxide is a triacid base, it must be capable of dissociating as follows: —

$$Al(OH)_3 = \overset{+++}{Al}, \overset{-}{OH}, \overset{-}{OH}, \overset{-}{OH}.$$

Aluminium hydroxide also acts as an acid towards strong bases. When aluminium hydroxide is treated with a strong base like sodium hydroxide, the following reaction takes place: —

$$Al(OH)_3 + 3\,NaOH = 3\,H_2O + Na_3AlO_3.$$

This compound, known as *sodium aluminate*, is obviously the sodium salt of the acid H_3AlO_3. The question which arises here is, How can a compound which dissociates like aluminium hydroxide, yielding hydroxyl ions, have acid properties or yield hydrogen ions? The dissociation of aluminium hydroxide depends upon the nature of the substance with which it is in contact. When in contact with an acid or hydrogen ions, it dissociates as indicated above, yielding hydroxyl ions. When in contact with a base or hydroxyl ions, it dissociates as follows: —

$$Al(OH)_3 = \overset{+}{H},\ H_2\overset{-}{Al}O_3,$$

$$H_2\overset{-}{Al}O_3 = \overset{+}{H},\ H\overset{=}{Al}O_3,$$

$$H\overset{=}{Al}O_3 = \overset{+}{H},\ \overset{\equiv}{Al}O_3.$$

In a word, it dissociates as a tribasic acid. We have seen a similar phenomenon manifested by zinc, and other cases will appear later.

Aluminates. — The compounds in which aluminium hydroxide plays the rôle of an acid are known as aluminates. There are three classes of these substances, as would be expected from the above described dissociation of aluminium hydroxide. Thus, we would have MH_2AlO_3, M_2HAlO_3, and M_3AlO_3, where M is a univalent ion. The alkali salts are soluble in water, showing an alkaline reaction. This is due to the hydrolysis of the aluminates by water, aluminium hydroxide being a weak acid as well as a weak base. The potassium salt most readily formed has the composition KH_2AlO_3 minus water, or $KAlO_2$. This is the potassium salt of *metaaluminic acid*, $HAlO_2$, obtained from aluminic acid by loss of water: —

$$Al(OH)_3 = H_2O + HAlO_2.$$

The alkaline earths also form aluminates. Those of barium are soluble in water, while those of calcium are insoluble. Calcium forms the normal aluminate $Ca_3(AlO_3)_2$, and also the metaaluminate $Ca(AlO_2)_2$. Since these salts harden in contact with water, they are used in connection with the preparation of *hydraulic cements*.

Magnesium forms a metaaluminate, which is the well-known mineral *spinel*. It has the composition $Mg(AlO_2)_2$. *Gahnite* is the corresponding zinc salt, $Zn(AlO_2)_2$, while *chrysobèryl* is the corresponding compound of glucinum, $Gl(AlO_2)_2$, and ferrous iron forms the metaaluminate-*pleonast*, $Fe(AlO_2)_2$.

We have a large number of minerals of the type of spinel, in which the place of the aluminium is taken by manganese, iron, etc. These will be referred to again.

The naturally occurring aluminates are frequently very stable compounds, requiring vigorous chemical reagents to decompose them. This is of importance in connection with the analysis of these minerals. They must be powdered very finely and fused with acid potassium sulphate, sodium carbonate, etc., before they can be gotten into solution.

Aluminium Chloride, $AlCl_3$, is formed when aluminium hydroxide is treated with hydrochloric acid. From such a solution it can be obtained in crystalline form with six molecules of water — $AlCl_3 . 6\,H_2O$.

The anhydrous chloride is obtained by heating aluminium filings in a current of dry, hydrochloric acid gas. It is also obtained by the action of chlorine on a mixture of aluminium oxide and carbon heated to a high temperature: —

$$Al_2O_3 + 3\,C + 3\,Cl_2 = 3\,CO + 2\,AlCl_3.$$

When the hydrated salt is heated it loses hydrochloric acid, and aluminium oxide remains behind: —

$$2\,AlCl_3 + 3\,H_2O = 6\,HCl + Al_2O_3.$$

Aluminium chloride is very hygroscopic, taking up moisture readily from the air when brought in contact with it.

With chlorides of the alkalies it forms beautifully crystalline double salts, which are quite stable. The sodium aluminium chloride volatilizes without decomposition.

Aluminium chloride is strongly hydrolyzed by water, aluminium hydroxide being precipitated: —

$$AlCl_3 + 3\,H_2O = 3\,HCl + Al(OH)_3.$$

This can be prevented by adding hydrochloric acid to the solution. By sufficiently increasing the mass of this acid, the reverse reaction involving the reformation of aluminium chloride can be carried very nearly to the limit; so that there is only an infinitesimal amount of the hydroxide formed.

Aluminium chloride has the remarkable property of causing hydrogen in one compound to combine with chlorine in another, forming hydrochloric acid; the residues of the two substances uniting and forming a new compound. This reaction, known as the *Friedel-Crafts reaction*, is of great importance in organic chemistry for effecting the synthesis of many well-known substances.

The molecular weight of aluminium chloride can be readily

determined from its vapor-density. Determinations of the density at 440° — just above the boiling-point — showed a molecular weight corresponding to the formula Al_2Cl_6. The vapor-density determinations made by Nilson and Pettersson at much higher temperatures (up to 1300°) gave a molecular weight corresponding to the formula $AlCl_3$.

From these investigations it seems highly probable that in the vapor of aluminium chloride, just above its boiling-point, the double molecules exist, while at higher temperatures these break down into the simplest molecules, $AlCl_3$.

The *fluoride of aluminium*, or *cryolite*, has already been referred to as occurring in Greenland, and as having the composition Na_3AlF_6. It is obviously the sodium salt of *hydrofluoraluminic acid*, H_3AlF_6. When cryolite is fused with lime the following reaction takes place: —

$$Na_3AlF_6 + 3\,CaO = 3\,CaF_2 + Na_3AlO_3.$$

When carbon dioxide is passed into the aqueous solution of sodium aluminate, sodium carbonate and aluminium hydroxide are formed: —

$$2\,Na_3AlO_3 + 3\,CO_2 + 3\,H_2O = 2\,Al(OH)_3 + 3\,Na_2CO_3.$$

Cryolite is thus used for the preparation of sodium carbonate.

Aluminium Sulphide, Al_2S_3, is formed by heating aluminium hydroxide in the vapor of carbon disulphide. It is decomposed by water, and even by the moisture in the air, into aluminium hydroxide and hydrogen sulphide: —

$$Al_2S_3 + 6\,H_2O = 3\,H_2S + 2\,Al(OH)_3.$$

This explains why aluminium sulphide is not formed when hydrogen sulphide is passed through a solution of an aluminium salt. The corresponding hydroxide is thrown down under these conditions: —

$$2\,AlCl_3 + 3\,H_2S + 6\,H_2O = 2\,Al(OH)_3 + 6\,HCl + 3\,H_2S.$$

This is the first metal sulphide which we have thus far encountered that is decomposed by water.

Aluminium Sulphate, $Al_2(SO_4)_3 . 18\,H_2O$, is formed by treating aluminium hydroxide with sulphuric acid and heating the mixture. On evaporating the solution, a salt of the above composition separates. It is also formed by treating clay with concentrated sulphuric acid and purifying the product. Aluminium sulphate is

hydrolyzed by water, as we would expect, on account of aluminium being such a weak base. The solution contains free hydrogen ions and, therefore, reacts acid. Aluminium sulphate forms with sulphuric acid a basic sulphate in which only one hydroxyl of the aluminium hydroxide has disappeared. This has the composition $(Al(OH)_2)_2SO_4 . 7\ H_2O$. When we consider that aluminium hydroxide is such a weak base and sulphuric acid a strong acid, it is surprising that such a compound should exist. This basic sulphate occurs in nature under the name of *aluminite.*

The Alums. — Aluminium sulphate combines with the sulphates of the alkalies to a remarkable extent, forming a class of double sulphates known as the alums. These have the general composition, $MAl(SO_4)_2 . 12\ H_2O$, in which M is an alkali ion. There are a large number of these substances; indeed, every alkali sulphate forms an alum with aluminium sulphate. The best known of these are potassium alum, $KAl(SO_4)_2 . 12\ H_2O$, and ammonium alum $NH_4Al(SO_4)_2 . 12\ H_2O$. The alums all crystallize in the same system, as octahedra and cubes, and are all *isomorphous*, *i.e.* will form crystals containing several of these substances. When a crystal of one alum is suspended in a solution of another alum, the second alum will be deposited upon it as upon one of its own crystals.

The term alum has been extended from the double sulphates of aluminium and the alkalies, to the double sulphates of allied elements and the alkalies. Thus, we have a series of iron alums of the general composition, $MFe(SO_4)_2 . 12\ H_2O$, in which M is sodium, potassium, rubidium, cæsium, lithium, or ammonium. Similarly, we have a series of manganese alums, $M_1Mn(SO_4)_2 . 12\ H_2O$, and a series of chromium alums, $MCr(SO_4)_2 . 12\ H_2O$. These all crystallize in the regular system, contain twelve molecules of water of crystallization, and are isomorphous with one another and with the corresponding aluminium compounds.

When alum is heated it passes into solution in its water of crystallization, and when heated higher loses its water, swells up, and forms a light powder which is known as *burnt alum.*

Alum, which is easily prepared by bringing the two sulphates together in solution and evaporating the solution to crystallization, is used to-day very largely in sizing paper, and as a *mordant* in dyeing. Aluminium compounds, as we have seen, are hydrolyzed to some extent by water. The aluminium hydroxide formed unites firmly with the fibre of the substance to be dyed, and also unites with the dye. In this manner a mordant renders the object permanently dyed.

The sodium alum is much more soluble than the potassium or ammonium alum, while the rubidium alum is much less soluble.

These complex sulphates dissociate in dilute solutions just like the constituent sulphates. A dilute solution of an alum has, then, the same properties as a mixture of the two sulphates. This is shown by determining the conductivity of solutions of alum. It is the same in dilute solution as the mixture of the two sulphates. In concentrated solution the conductivity of the alum is less than that of the mixed sulphates, showing that some of the complex ions persist undecomposed in such solutions.

Aluminium Carbide (Al_4C_3) and Carbonate. — Aluminium combines with carbon, forming the carbide, Al_4C_3. This was produced by Moissan, by heating aluminium in carbon boats in an electric furnace, also in preparing aluminium by the electrolytic method where the metal separates upon carbon electrodes.

Aluminium carbide decomposes with water forming methane and aluminium hydroxide: —

$$Al_4C_3 + 12\,H_2O = 4\,Al(OH)_3 + 3\,CH_4$$

The carbonate of aluminium can exist only at low temperatures. Even at ordinary temperatures it decomposes into the hydroxide and carbon dioxide. When a soluble carbonate is added to a solution of an aluminium salt, the hydroxide and not the carbonate is precipitated: —

$$2\,AlCl_3 + 3\,Na_2CO_3 + 3\,H_2O = 6\,NaCl + 3\,CO_2 + 2\,Al(OH)_3.$$

Silicates of Aluminium. — These are very important substances. Aluminium forms salts not only with normal silicic acid, but with the polysilicic acids. A salt of the composition Al_2SiO_5 is known as *disthene*. A comparatively pure form of aluminium silicate is known as *kaolin*. This substance has approximately the composition $Al_4(SiO_4)_3.4\,H_2O$, being the aluminium salt of normal silicic acid.

Clay is an impure variety of aluminium silicate. This is formed as the result of the weathering of the rocks, and, consequently, many other substances are liable to be present in it. The different colors of clays are due to different impurities.

Marl is clay containing a large amount of calcium carbonate.

Aluminium silicate readily forms *double silicates* with the silicates of the alkalies, and these constitute some of the most important minerals, the *feldspars*. We have potassium feldspars, sodium feldspars, potassium sodium feldspars, etc. These have the general

composition $MAlSi_3O_8$. The potassium feldspar is known as *orthoclase*, the sodium compound as *albite*. The feldspars are continually undergoing decomposition, affected by the moisture and carbon dioxide in the air, and they are the chief source of the soluble potassium compounds in the soil. This is one important effect of that geological process known as weathering which is going on over the surface of the earth.

Aluminium silicate forms double silicates with many other elements, especially with those of the calcium and iron group. Among the double silicates of aluminium are such minerals as the *garnets*, *mica*, *zeolites*, etc.

Lapis lazuli is a double silicate of sodium and aluminium, containing sulphur. It is a beautiful coloring matter known under the name of *ultramarine*. This substance is also prepared artificially for commercial purposes.

Applications of Aluminium Silicates. — When kaolin, clay, or marl is mixed with water it forms a thick, viscous mass, which can be readily moulded or worked into any desired form. When this mass is dried and heated it becomes very hard and then resists the action of water. It is from this material that ordinary *brick* or *fire-brick* is made.

Earthenware or *stoneware* is made from a somewhat purer variety of aluminium silicate than that employed in the manufacture of ordinary fire-brick. The objects are moulded from the purer varieties of clay or kaolin by mixing with water to the proper consistency. They are then "fired" or "baked" by heating to a high temperature. The resulting objects are, however, very porous, and would be comparatively useless in this form. They must be covered by a non-porous material — must be *glazed*. There are different methods of glazing such objects. A mixture of kaolin and feldspar melts at a comparatively low temperature, and this is sometimes applied to the surface of earthenware after it has been "burned," and the object then reheated. This method is seldom applied to ordinary earthenware. After the earthenware has been burned, sodium chloride is thrown into the furnace. This is decomposed at the high temperature by the water-vapor, and forms hydrochloric acid which escapes, and sodium hydroxide — it is hydrolyzed. The sodium hydroxide then acts on the silicate of aluminium, forming the double silicate of sodium and aluminium, which fuses and forms a glassy, impervious coating over the porous earthenware.

Porcelain is made of pure aluminium silicate or pure kaolin. This is mixed in definite proportions with feldspar to lower its melt-

ing-point, and also with quartz. The mixture is treated with water until the desired consistency is reached, and is then moulded into the desired form. It is then dried and "burned." The glaze consists of a mixture of feldspar, quartz, and lime. After applying the glaze the vessel is heated again to a very high temperature. The many different varieties of porcelain owe their peculiar characteristics in part to the nature of the materials used, and in part to the way in which they are manipulated during manufacture.

Aluminium silicate is also an important constituent of many valuable *cements.*

Detection of Aluminium.—Aluminium belongs to that class of elements whose hydroxides are precipitated from an alkaline solution by hydrogen sulphide, or whose hydroxides are precipitated from a neutral solution by ammonium sulphide.

SCANDIUM (At. Wt. = 44.1)

The special interest connected with the element scandium has to do with its relation to the Periodic System of the elements. Mendeléeff, in 1869, predicted the existence of an element with an atomic weight of 44, occupying a position in the Periodic System next to boron in group III. He termed the element *ekaboron.* This element was discovered by the Swedish chemist, Nilson, in 1879, in certain Norwegian minerals,—*gadolinite, euxenite,* etc.,—and named scandium from the locality in which it was found.

The properties of the element, and especially of its compounds, were predicted in detail by Mendeléeff, and his predictions have been verified to a surprising extent.

Scandium forms the oxide Sc_2O_3 and the hydroxide $Sc(OH)_3$. The nitrate has the composition $Sc(NO_3)_3$, and the sulphate $Sc_2(SO_4)_3 . 6\,H_2O$. Scandium forms a double sulphate with the sulphate of potassium, having the composition $3\,K_2SO_4 . Sc_2(SO_4)_3$.

GALLIUM (At. Wt. = 70.0)

Gallium has the same interest in connection with the Periodic System as scandium. Its existence and properties were predicted by Mendeléeff in 1869. He placed it in his system next to aluminium and termed it *ekaaluminium.* It was discovered by Lecoq de Boisbaudran in 1875, in certain zinc blendes which occur at Pierrefitte, in France, and named for the country from which it came. It occurs in extremely small quantities in these ores, and its presence was

detected by means of the spectroscope. It forms compounds of the general type GaA_3, where A is a univalent anion. Thus, we have $Ga(NO_3)_3$, $GaCl_3$, $Ga_2(SO_4)_3$, Ga_2O_3, and so on. Gallium can also form gallous compounds — $GaCl_2$.

YTTRIUM (At. Wt. = 89.0)

Yttrium also occurs in the Norwegian minerals, *gadolinite*, *yttria·lite*, *euxenite*, etc., and in *monazite sand*. It resembles the other members of the group, forming compounds of the general type YA_3, A being a univalent anion. Thus we have $Y(NO_3)_3$, $Y_2(SO_4)_3$, Y_2O_3, and so on.

INDIUM (At. Wt. = 115.0)

Indium occurs in certain zinc blendes in Freiberg, but in very small quantities. It forms compounds which are analogous to those of aluminium. Thus we have, $InCl_3$, $In(NO_3)_3$, $In_2(SO_4)_3$, $In(OH)_3$, In_2O_3.

LANTHANUM (At. Wt. = 138.9)

Lanthanum occurs in *cerite*, *samarskite*, *monazite sand*, etc. It forms La_2O_3, $La(NO_3)_3$, $LaCl_3$, $La_2(SO_4)_3$. It has been prepared as the double nitrate with ammonium in considerable quantity in connection with the manufacture of Welsbach lights. The Welsbach Light Co. of Gloucester, New Jersey, owns several hundred pounds of the almost pure nitrate of lanthanum and ammonium.

YTTERBRIUM (At. Wt. = 173.0)

Ytterbrium is found especially in the mineral *euxenite*. It forms the oxide Yt_2O_3, and the salts have the same general composition as those of the other rare elements just considered.

THALLIUM (At. Wt. = 204.1)

Thallium occurs in a number of minerals, but always in limited quantities. Its chief source is certain zinc blendes. When these are roasted the thallium passes off and is deposited in the dust in the flues, and it was here that it was first discovered by Crookes in 1861, by means of the spectroscope. Its spectrum is characterized by a bright green line, whence the name of the element.

Thallium forms two classes of compounds — the thallous and the thallic. In the former the thallium is univalent, in the latter trivalent. Among the thallous salts are the chloride TlCl, the bromide

TlBr, the iodide TlI, and the sulphide Tl_2S. Thallous chloride is difficultly soluble in water, resembling in this particular the element lead. The bromide is less soluble, and the iodide the least soluble of the three. Among the thallic compounds are the chloride $TlCl_3$, the carbonate $Tl_2(CO_3)_3$, the sulphide Tl_2S_3, and so on. Thallous thallium resembles in many respects potassium, forming salts which are often isomorphous with the corresponding potassium compounds. Thallic thallium resembles aluminium and the rare elements which we have just been considering.

SAMARIUM (At. Wt = 150.3)

The position of this element in the Periodic System is not yet fixed. It occurs in the mineral *thorite*, and in some respects resembles aluminium. It forms the oxide Sa_2O_3, which is a weak base, dissolving in acids. Its salts have a sweet taste.

CHAPTER XXXIII

IRON, COBALT, NICKEL, MANGANESE, CHROMIUM, MOLYBDANUM, TUNGSTEN, URANIUM

IRON (At. Wt. = 55.9)

We now come to a group which contains some of the most important elements technically, as well as some of the most interesting from the chemical standpoint. The first of these, and the one from which the group takes its name, is iron — the most important technically of all the elements.

Occurrence and Preparation. — Iron occurs very widely distributed in nature, but not in abundance in the free state. This is due especially to its action on water forming the hydroxide. Iron, however, occurs in the uncombined condition in certain meteorites and in certain localities, as at Ofvivak, Greenland. Iron occurs chiefly in the form of oxides and sulphides. It occurs in large quantities as *magnetite*, Fe_3O_4, as *hematite*, Fe_2O_3, and as *bog-iron ore*, *limonite*, and other hydroxides. Iron also occurs in large quantities as *pyrites*, FeS_2, and as the carbonate, $FeCO_3$, or *siderite*.

Iron is prepared by reduction of its oxides by carbon: —

$$Fe_2O_3 + 3\,C = 3\,CO + 2\,Fe,$$
$$Fe_3O_4 + 4\,C = 4\,CO + 3\,Fe.$$

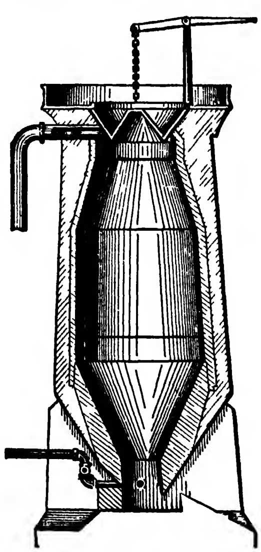


FIG. 41.

In preparing iron on the commercial scale the "blast furnace" is employed. This is shown in Fig. 41. The furnace consists of an iron case lined on the inside with fire-brick, and has the shape shown in the figure. It is provided with pipes at the bottom for introducing hot air under pressure, and with pipes at the top for carrying off the gaseous products of combustion. These furnaces are often quite large, being as much as eighty feet

high. They are filled with coal or coke, the ore, and a flux, which are mixed when introduced into the furnace. The nature of the flux, which is used to protect the metal when formed, depends upon the impurities contained in the ore. If there is much silica in the ore, limestone is used as the flux. If there is much calcium or magnesium in the ore, a flux containing silica (sand) or aluminium (feldspar) is employed. Limestone, however, is almost always used as the flux in the blast furnace.

The oxide of iron is reduced to the metal by means of the highly heated carbon and the carbon monoxide formed as the product of the combustion of the carbon. The combustion of the carbon is increased by blowing hot air under pressure into the bottom of the furnaces. Much of the carbon monoxide is not oxidized by the iron oxide to carbon dioxide, and escapes at the top of the furnace through tubes provided to receive it, and is used as fuel.

The operation of a blast furnace is continuous; alternate charges of coke, ore, and flux are being continually added at the top of the furnace, and the molten metal and the slag drawn off at the bottom. The molten metal coming in contact with the hot carbon dissolves a part of it, and iron thus prepared always contains some carbon, as well as silicon and other substances, dissolved in it. The iron is run into moulds made in the sand, and this impure product is known as *pig-iron*, or cast-iron.

Properties of Iron. — Pure iron is light gray in color, can readily be drawn into wire, hammered or rolled into sheets. At a bright-red heat it can be *welded*, or one piece made to adhere to another by simply hammering the two together. Iron is a good conductor of heat and electricity, and is one of the most resistant to strain of all the metals. It is this property, together with its great abundance and the ease with which it can be prepared, that makes it the most valuable commercially of all the metals.

When iron is heated in the presence of the air, it readily burns, uniting with oxygen and forming one of the oxides of iron. Iron acts upon moist air even at ordinary temperatures, but acts slowly. This is known as the *rusting of iron*. It does not act appreciably upon dry air. Iron acts upon water at all temperatures, forming the hydroxide: —

$$2\,Fe + 6\,H_2O = 2\,Fe(OH)_3 + 3\,H_2.$$

While the action is slow at ordinary temperatures, it is rapid when steam is passed over red-hot iron.

Iron dissolves readily in dilute acids, liberating hydrogen and

combining with the anion of the acid, forming the corresponding salt. As we have seen, this is the same as to say that the hydrogen ions give up their charges to the iron atoms, converting them into ions, the hydrogen ions becoming atoms.

When iron is dipped into very strong nitric acid and then into dilute, the latter is without action upon it. The iron is then in the *passive condition.* This has recently been shown to be due to an electrical condition of the metal, and not to the formation of a protecting layer of oxide over its surface as was formerly supposed.

Impure or Commercial Iron.—The different varieties of iron which are used commercially have very different properties. These are due to the different amounts of impurities in the iron. We have already seen how *pig-iron* or *cast-iron* is made. Cast-iron is very impure, containing in addition to from 3 to 4 per cent of carbon, 1 or more per cent of silicon, besides phosphorus, manganese, sulphur, etc. If there is considerable silicon present, and the cast-iron cools slowly, the carbon separates largely as graphite, and gives a gray cast to the iron. This is known as *gray cast-iron.* If the iron is cooled rapidly the carbon remains largely in chemical combination with the iron. Such iron is light in color and is known as *chilled cast-iron.*

White cast-iron contains no graphite. It usually contains less silicon or more manganese or sulphur than any gray cast-iron.

Cast-iron in general contains from 4 to 5 per cent of carbon, and melts at a much lower temperature than pure iron. It is, therefore, easily moulded, and gray cast-iron is used extensively for making objects where great strength is not required. Cast-iron is brittle and readily broken by a jar, and is far less tough than pure iron. Cast-iron is not malleable, since it is too brittle, and although it melts lower than pure iron, does not appreciably soften before it melts. It therefore cannot be welded like pure iron.

If the ore from which the iron is made is rich in manganese, the final product is also rich in manganese, and usually contains more carbon than ordinary cast-iron. This is known as *spiegel iron,* and contains from 10 to 15 per cent of manganese and in some cases even more.

When most of the impurities have been removed from iron we have *wrought-iron.* This still contains a small amount of carbon, the amount, however, usually being less than one-half of one per cent. Wrought-iron has very different properties from cast-iron. It is very tough, strong, and malleable. It melts at about 2000°, but becomes soft at a bright-red heat, so that it can be hammered, rolled, or welded. Wrought-iron, while extremely tough, is comparatively

soft, and bends easily under strain. It is, therefore, not as useful as a form of iron which contains more carbon, and is known as steel.

Steel is usually iron practically free from all impurities except carbon, which is present to from 0.8 to 2 per cent. There are two general methods by which steel may be made, — either by removing carbon and other impurities from cast-iron, or by adding carbon to wrought-iron. The former process would seem to be the simpler, since it is necessary to remove the carbon from cast-iron in order to obtain wrought-iron. The latter process, however, is the one most frequently made use of. A few methods of making steel are so important commercially and are so frequently referred to that they will be briefly described.

The Bessemer Converter consists of a pear-shaped vessel of malleable iron, lined on the inside with refractory material. The molten cast-iron is poured into the converter, and compressed air forced through the molten metal. The carbon and silicon are completely oxidized by the oxygen of the air, and the product is similar in composition to wrought-iron. This is kept above its melting-point by the heat of combustion of the carbon and silicon. In order to obtain a product with the desired amount of carbon, spiegel iron is added in quantity sufficient to bring the percentage of carbon up to the desired amount. The product is *Bessemer steel,* which has found such extensive application in the arts.

The Siemens-Martin Process of making steel consists in heating a mixture of wrought-iron which contains but little carbon with pig-iron, iron ore being sometimes added. The gas used as fuel is previously heated.

The Thomas-Gilchrist Converter. — The Bessemer process of making steel does not remove the phosphorus from the iron. The presence of an appreciable amount of phosphorus so changes the properties of the steel as to render it entirely unfit for certain purposes. While they were dependent solely upon the Bessemer or similar processes, only certain iron ores which contain only a small amount of phosphorus could be used for making steel. This has largely been changed, due to the Thomas-Gilchrist converter. This is essentially a Bessemer converter lined with burned dolomite, which is a mixture of lime and magnesia. This "basic lining," as it is termed, unites with the phosphoric acid formed by the oxidation of the phosphorus by the oxygen of the air which is blown through the molten iron, and forms calcium and magnesium phosphates. This material, known as the "Thomas slag," is extensively used as a source of phosphoric acid in commercial fertilizers, having a com-

position very similar to the "phosphate rock," which is so extensively used as a fertilizer in the manner already described (p. 372).

Steel is useful largely because it can be made to assume any degree of hardness. When allowed to cool very slowly ordinary steel is soft and resembles wrought-iron in its properties. When highly heated and made to cool rapidly steel becomes very hard and brittle, the degree of hardness depending somewhat upon the amount of carbon present. The process by which the hardness of steel is regulated is known as *tempering*. The steel is heated moderately, the temperature being estimated by the color of the layer of oxide which forms on the bright surface. This color is due to interference, like the color of thin plates. The steel is then cooled more or less slowly.

Oxides of Iron. — Iron forms two well-known oxides, Fe_2O_3, or *hematite*, and Fe_3O_4, or *magnetite*.

Magnetite or magnetic iron ore is so called because it is strongly magnetic. It is formed by burning iron in oxygen. As it occurs in nature it is often beautifully crystalline, forming almost perfect octahedra and cubes. It is sometimes regarded as the ferrous salt of the hypothetical acid, $HFeO_2 - FeFe_2O_4$.

Ordinary ferric oxide, Fe_2O_3, occurs in nature in great abundance as hematite. It is also formed when a ferric salt or ferric hydroxide is heated. In the form of a fine powder it is known as *rouge*, which, on account of its color, is used as a pigment, and on account of its fine state of division as a polish, where a very highly polished surface is desired.

When ferric oxide is reduced by carbon monoxide, black ferrous oxide, FeO, is formed.

Ferrous and Ferric Compounds. — Iron forms two kinds of ions, — one carrying two electrical charges and known as the ferrous ion, $\overset{++}{Fe}$, and the other carrying three electrical charges and known as the ferric ion, $\overset{+++}{Fe}$. These are what have hitherto been described as the ferrous and the ferric condition. In the case of iron we can verify the statement that Faraday's law is the base of chemical valence. If a given electric current is passed through a solution of a ferrous, and a solution of a ferric salt, one and one-half times as much iron will separate from the ferrous solution as from the ferric. By comparing the amount of iron which separates from a ferrous solution with the amount of a univalent metal separated by the same current, it can be shown that ferrous iron ($\overset{++}{Fe}$) is bivalent, or that the ferrous ion carries two charges of electricity. The ferric ion $\overset{+++}{Fe}$ is, therefore, trivalent, or carries three charges of electricity.

We shall see that a ferrous ion can be converted into a ferric ion by oxidation, as it is said, and a ferric ion converted into a ferrous ion by reduction. All that takes place when a ferrous ion is converted into a ferric ion is the addition of one electrical charge, and the removal of one electrical charge from a ferric ion converts it into a ferrous ion. Oxidation and reduction as used in this sense are simply the addition or removal of electrical energy, and, like valence, have their physical basis in Faraday's law.

Ferrous ($Fe(OH)_2$) and Ferric ($Fe(OH)_3$) Hydroxides. — The two conditions described above are exemplified in the hydroxyl compounds of iron. In one of these the iron holds two hydroxyl groups in combination; in the other, three. Ferrous hydroxide is precipitated when an alkali is added to a solution of a ferrous salt: —

$$FeCl_2 + 2\,NaOH = 2\,NaCl + Fe(OH)_2.$$

Ferrous hydroxide is white, but unites rapidly with the oxygen of the air forming ferric hydroxide, which then reacts with ferrous hydroxide, forming the black magnetite, or a hydroxide of this substance: —

$$2\,Fe(OH)_3 + Fe(OH)_2 = FeFe_2O_4 + 4\,H_2O.$$

This black substance, in the finely divided condition, mixed with the white, ferrous hydroxide, gives it the well-known green appearance.

Ferrous hydroxide dissolves readily in acids, forming solutions of ferrous salts. It does not dissolve in bases.

Ferric hydroxide is formed when an alkali is added to a solution of a ferric salt: —

$$FeCl_3 + 3\,NaOH = 3\,NaCl + Fe(OH)_3.$$

It is a reddish-brown precipitate, readily soluble in acids, forming solutions of ferric salts. Unlike aluminium hydroxide, it does not dissolve in an excess of the base unless the latter is very concentrated.

Ferric hydroxide, when freshly precipitated, dissolves readily in a solution of ferric chloride. Since ferric hydroxide is a weak base its salts are readily hydrolized.

If the hydrochloric acid is allowed to diffuse through a membrane as it is set free from the salt, the decomposition of the salt will, in time, become practically complete. By *dialysis*, it is then possible to decompose ferric chloride practically completely. The ferric hydroxide, however, remains in solution, forming a dark-red liquid. This liquid has the characteristic properties of a *colloidal solution*, and is probably ferric hydroxide in a very fine state of division.

Ferrous ($FeCl_2$) and Ferric ($FeCl_3$) Chlorides. — Ferrous chloride is obtained when iron is treated with hydrochloric acid. It forms crystals containing four molecules of water, $FeCl_2 . 4\,H_2O$. The salt with water of crystallization is green in color. The white anhydrous salt is formed by heating iron in a current of hydrochloric acid gas. It forms double salts with the alkaline chlorides.

Ferric chloride is formed by passing chlorine over iron. It is also formed by passing chlorine into a solution of ferrous chloride. This reaction is of interest as illustrating a new method of ion formation. Ferrous chloride in solution is dissociated into a ferrous ion and chlorine ions, $\overset{++}{Fe}, \overset{-}{Cl}, \overset{-}{Cl}$.

Chlorine in solution in water is not dissociated. In the presence of an iron cation with two electrical charges, which can take up a third positive charge, the chlorine dissociates forming the corresponding anion. The above reaction is then to be represented for simplicity as follows, disregarding the fact that the chlorine molecule is made up of two atoms: —

$$\overset{++}{Fe}, \overset{-}{Cl}, \overset{-}{Cl} + Cl = \overset{+++}{Fe}, \overset{-}{Cl}, \overset{-}{Cl}, \overset{-}{Cl}.$$

A cation takes up another charge converting an atom into an anion. This is a method of ion formation not infrequently met with. Ferric chloride crystallizes from aqueous solution with six molecules of water, $FeCl_3 . 6\,H_2O$. Its vapor-density shows that the molecule is $FeCl_3$. It is readily transformed into ferrous chloride by reducing agents.

Chemical Action at a Distance. — Ferrous chloride can be oxidized to ferric chloride without the chlorine coming in contact with the ferrous salt. The beaker containing a solution of ferrous chloride is connected by means of a siphon with a beaker filled with a solution of potassium chloride, into which chlorine gas has been conducted. The siphon is filled with a solution of potassium chloride free from chlorine, so that no free chlorine comes in contact with the ferrous chloride. A platinum electrode is immersed in each beaker and the circuit closed. The current flows from the ferrous chloride to the solution of chlorine in potassium chloride. The iron takes up another charge of electricity from the electrode, passing into the ferric condition, and we have chlorine atoms on the other side of the cell passing over into ions. The result is the transformation of ferrous into ferric chloride, effected by chlorine which is not in contact with the ferrous salt. As the current flows the iron moves with the current over into the solution of chlorine, and the chlorine moves

against the current over into the solution of the ferrous salt. This, however, is a secondary act, the oxidation being effected right around the platinum pole immersed in the solution of the ferrous salt.

Sulphides of Iron. — When iron filings and sulphur are heated together the two combine and form *ferrous sulphide*, FeS. It is also formed by the action of ammonium sulphide on a ferrous salt. Heated in contact with the air it forms ferrous sulphate. Treated with acids hydrogen sulphide is liberated.

Ferric sulphide or iron sesquisulphide, Fe_2S_3, is formed by heating ferrous sulphide with sulphur. It is also formed when hydrogen sulphide is passed over iron heated to about 100°. *Iron disulphide*, FeS_2, is the familiar substance *pyrites*, which occurs so widely distributed in nature and in great abundance. On account of its color it is frequently taken for gold, and hence has acquired the name of *fool's gold*. It can be prepared by passing hydrogen sulphide over iron oxide heated to a temperature somewhat above 100°.

Ferrous Sulphate, $FeSO_4 . 7\,H_2O$. — Ferrous sulphate, also called "iron vitriol" on account of its composition, or "green vitriol" on account of its color, is the most important ferrous compound. It is formed by the action of sulphuric acid on iron or iron sulphide. It is made commercially by allowing ferrous sulphide to take up oxygen from the air. If pyrites is used, one-half of the sulphur is roasted out, and the ferrous sulphide is then moistened and allowed to take up oxygen from the air: —

$$FeS + 2\,O_2 = FeSO_4.$$

The salt is then extracted with water. Ferrous sulphate forms light-green crystals, and is extensively used in dyeing, in pharmacy, and as a disinfectant.

Ferrous sulphate, like other sulphates already studied, gives up six molecules of water at a comparatively low temperature. The last molecule is not set free until a temperature of about 300° is reached. If ferrous sulphate is allowed to crystallize from a solution at 80°, the salt which comes down contains only four molecules of water — $FeSO_4 . 4\,H_2O$. Ferrous sulphate readily forms double salts with the alkaline sulphates.

Ferric Sulphate, $Fe_2(SO_4)_3$, is formed by dissolving ferric oxide or hydroxide in sulphuric acid: —

$$2\,Fe(OH)_3 + 3\,H_2SO_4 = Fe_2(SO_4)_3 + 6\,H_2O.$$

It is also formed by the addition of a half-equivalent of sulphuric acid to ferrous sulphate, in the presence of an oxidizing agent like nitric acid. Ferric sulphate forms double sulphates with the alkali

sulphates, which, in composition and crystalline form resemble the aluminium alums, and are termed *iron alums.*

Potassium Ferrocyanide, $K_4Fe(CN)_6$. — Although iron does not combine directly with the cyanogen ion and form cyanides, it forms double cyanides which are beautifully crystallized compounds. When potassium cyanide is allowed to act upon iron in the presence of water the following reaction takes place: —

$$Fe + 6\,KCN + 2\,H_2O = 2\,KOH + H_2 + K_4Fe(CN)_6.$$

Potassium ferrocyanide is usually formed by heating nitrogenous matter with iron filings and potash. When the mass is digested with water and the solution evaporated, beautiful yellow crystals are formed, having the composition $K_4Fe(CN)_6.3\,H_2O$. This is potassium ferrocyanide, known commercially as *yellow prussiate of potash.*

When this compound is heated it is decomposed into potassium cyanide, iron carbide FeC_2, and nitrogen. When it is treated with a strong acid a white solid is thrown down: —

$$K_4Fe(CN)_6 + 4\,HCl = 4\,KCl + H_4Fe(CN)_6.$$

This substance, $H_4Fe(CN)_6$, *hydroferrocyanic acid,* is the acid of which potassium ferrocyanide is the salt. It dissolves in water, forming a strongly acid solution. This fact, together with the composition of the potassium salt, shows that it is dissociated by water in the following manner: —

$$H_4Fe(CN)_6 = \overset{+}{H}, \overset{+}{H}, \overset{+}{H}, \overset{+}{H}, Fe(\overset{\equiv}{C}N)_6.$$

The anion of this acid is interesting on account of its composition. In addition to the six cyanogen groups, each of which carries a negative charge, it contains ferrous iron with two positive charges. The result is an anion with four negative charges. It is interesting to note also that a positively charged constituent (iron) may form a part of an anion. The iron in this complex anion has lost its characteristic properties, as we are accustomed to say; *i.e.* it no longer possesses the properties of iron when alone in the ferrous or ferric condition, nor is there any reason to expect that it should.

Hydroferrocyanic acid forms well-characterized salts. The most important of these is the ferric salt: —

$$3\,H_4Fe(CN)_6 + 4\,FeCl_3 = 12\,HCl + Fe_4(Fe(CN)_6)_3.$$

This is the well-known substance *Prussian blue* or *Berlin blue,* which is valuable as a pigment, and is formed whenever ferric ions come in contact with the anion of hydroferrocyanic acid, $Fe(\overset{\equiv}{C}N)_6$.

This reaction is, therefore, a *very sensitive test for the presence of ferric ions.*

The copper salt of this acid has acquired physical chemical distinction in connection with the demonstration and measurement of osmotic pressure. This substance is formed by the action of any soluble cupric salt upon potassium ferrocyanide in solution: —

$$K_4Fe(CN)_6 + 2\,CuSO_4 = Cu_2Fe(CN)_6 + 2\,K_2SO_4.$$

Copper ferrocyanide is a reddish-brown gelatinous solid, resembling in appearance ferric hydroxide. When deposited in the walls of porous cups it allows water to pass through but prevents the dissolved substance from passing. It is, therefore, used in the construction of *semi-permeable membranes.* Prussian blue has been used in the same connection but far less successfully. Calcium phosphate has also been used, but copper ferrocyanide gives by far the best results, as we have already seen.

Potassium Ferricyanide, $K_3Fe(CN)_6$, is formed by the action of oxidizing agents on potassium ferrocyanide. If chlorine is passed into a solution of potassium ferrocyanide, potassium ferricyanide is formed: —

$$2\,K_4Fe(CN)_6 + Cl_2 = 2\,KCl + 2\,K_3Fe(CN)_6.$$

The compound $K_3Fe(CN)_6$ is known also as *red prussiate of potash,* from the deep-red color of its crystals. When this compound is treated with an acid *hydroferricyanic acid* is liberated: —

$$K_3Fe(CN)_6 + 3\,HCl = 3\,KCl + H_3Fe(CN)_6.$$

This dissolves in water, dissociating as follows: —

$$H_3Fe(CN)_6 = \overset{+}{H}, \overset{+}{H}, \overset{+}{H}, Fe(\overset{\equiv}{C}N)_6.$$

The anion of this acid is the same in composition as the anion of hydroferrocyanic acid. The difference is that here the anion carries three electrical charges, while in the ferrocyanides it carries four. In the ferri compounds there are, therefore, three univalent cations, and in the ferro compounds four.

When a ferricyanide is treated with a ferrous salt, the ferrous compound of hydroferricyanic acid is formed: —

$$2\,K_3Fe(CN)_6 + 3\,FeCl_2 = 6\,KCl + Fe_3(Fe(CN)_6)_2.$$

This substance is known as *Turnbull's blue,* and this reaction is one of the most sensitive tests for ferrous ions.

Prussian blue and Turnbull's blue are interesting as showing the same metal in the same compound in two different ionic conditions.

In these compounds we have iron in the cationic condition, and also united with cyanogen as a part of an anion. The iron in the former condition shows the reactions which we are accustomed to ascribe to iron; the iron in combination with cyanogen in the anions does not show these reactions. This illustrates another fact, that the *reactions which we are accustomed to ascribe to an element are reactions of the ions of that element, and of the ions alone.*

Change in Color with Change in Electrical Charge. — An ion having the same chemical composition does not always have the same color. Take the ion $Fe(CN)_6$; in potassium ferrocyanide it is yellow and gives the yellow color to a solution of this salt. The ion in this case is formed by the dissociation of the salt $K_4Fe(CN)_6$ into $\overset{+}{K}$, $\overset{+}{K}$, $\overset{+}{K}$, $\overset{+}{K}$, and $Fe(\overset{\equiv}{\overline{C}}N)_6$, which carries four negative charges. The ion $Fe(CN)_6$, obtained by the dissociation of potassium ferricyanide, is red. The compound $K_3Fe(CN)_6$ dissociates as follows: —

$$K_3Fe(CN)_6 = \overset{+}{K}, \overset{+}{K}, \overset{+}{K}, Fe(\overset{\equiv}{C}N)_6.$$

The ion $Fe(\overset{\equiv}{C}N)_6$, in this case, carries three negative charges, and the difference of one charge changes the color of the ion from yellow to red.

To take a simpler example: The iron ion in the ferrous condition, $\overset{++}{Fe}$, is green, as is seen in solutions of ferrous salts; while the iron ion in the ferric condition, $\overset{+++}{Fe}$, is yellow, as is seen in solutions of ferric salts. A large number of examples of changes in the color of ions with change in the electrical charge which they carry, might be given.

Other Salts of Iron. — The ferric salt of sulpho-cyanic acid is of importance in connection with the detection of iron. *Ferric sulphocyanate*, $Fe(CNS)_3$, is deep blood-red in color when undissociated. A solution containing molecules of this substance has, therefore, a characteristic red color. Such a solution is prepared by adding to a ferric salt an excess of potassium sulpho-cyanate, which is the same as adding an excess of sulpho-cyanogen ions. In accordance with the general principle with which we are familiar, this would drive back the dissociation of the ferric salt and bring out the color of its molecules.

Sodium nitroprussiate, $Na_2Fe(CN)_5NO.2\,H_2O$, is formed by treating sodium ferrocyanide with nitric acid. It is useful in testing for the alkaline sulphides, with which it gives a purple color.

Iron like nickel combines with carbon monoxide forming *car-*

bonyl compounds. Several of these are known having the compositions $Fe(CO)_5$, $Fe(CO)_4$, etc.

Ferric Acetate, Fe $(CH_3COO)_3$, is deep red in solution, and is a fairly sensitive test for iron. Like the salts of weak acids in general it is hydrolized by water, and when its solution is boiled the basic acetate is precipitated. This is of importance in connection with the quantitative determination of iron.

Ferrates. — We have seen that aluminium can act as an acid-forming element, the hydroxide being soluble in sodium hydroxide. Iron can act in the same capacity, but as an acid-forming element has a valence of six. *Ferric acid* has the composition H_2FeO_4, and is, therefore, analogous to sulphuric acid, and, as we shall see, to chromic acid.

The potassium salt of this acid is formed by the action of strong oxidizing agents on iron, in the presence of potassium hydroxide. When iron oxide is treated with chlorine in the presence of potassium hydroxide, potassium ferrate, K_2FeO_4, is formed. This same compound is also formed when iron is heated with potassium nitrate. Other salts of ferric acid are known.

CHAPTER XXXIV

COBALT AND NICKEL

COBALT (At. Wt. = 59.0)

The chief sources of cobalt are the mineral *smaltite*, which is the arsenide of the composition $CoAs_2$, and the mineral *cobaltite*, which has the composition CoAsS. The element is prepared by reducing the oxide either with highly heated carbon, or with hydrogen. Cobalt resembles iron in many respects. It has a somewhat lighter color, with a distinctly reddish tint. It melts at about the same temperature as iron. It forms a coating of oxide in contact with moist air, but not with dry air. Like iron it decomposes water readily at a high temperature. It dissolves slowly in hydrochloric and sulphuric acids, and readily in nitric acid.

Cobaltous and Cobaltic Compounds. — Cobalt, like iron, forms two kinds of ions. The cobaltous ion $\overset{++}{Co}$, and the cobaltic ion $\overset{+++}{Co}$. Unlike iron, however, the cobaltous ion is the more stable condition, while the ferric condition is the more common for the iron ion. The cobaltous ion combines readily with the anions of acids, forming solutions of cobalt salts. The cobaltic ion also can form salts with certain anions, but the cobaltic condition is especially met with in complex compounds.

Oxides and Hydroxides of Cobalt. — Several oxides of cobalt are known. *Cobaltous oxide*, CoO, is formed when cobaltous carbonate or hydroxide is heated. It is a greenish powder, easily reducible to the metal. *Cobaltic oxide*, or *cobalt sesquioxide*, Co_2O_3, is formed by gently heating the nitrate. It is a dark-brown powder, which passes over, when heated, into *cobalto-cobaltic* oxide.

When a cobaltous salt is treated with an alkali, cobaltous hydroxide is formed: —

$$CoCl_2 + 2\,KOH = 2\,KCl + Co(OH)_2.$$

At first a basic salt which is blue is formed, but this gradually decomposes into the red hydroxide. Oxidizing agents readily convert this into *cobaltic hydroxide*, $Co(OH)_3$, which is black. Cobalt also

forms an acid which corresponds to the hydroxide $Co(OH)_4$ minus water — H_2CoO_3. Certain salts of this acid are known and are called *cobaltites.*

Cobaltous Salts. — When metallic cobalt is heated in chlorine, *cobalt chloride*, $COCl_2$, is formed. This crystallizes from an aqueous solution with six molecules of water — $CoCl_2.6\,H_2O$. The solution of the salt is red. When the water is removed the salt is deep blue in color, due to the driving back of the ions into molecules, which are blue. Cobalt chloride has, therefore, been used as *sympathetic ink.* When a solution of the salt is used for writing on paper, the writing is practically colorless, due to the nearly colorless nature of an aqueous solution of cobaltous chloride. When the paper is warmed the blue color appears, and the writing becomes plainly legible. When the blue material is allowed to stand in contact with the air, it takes up moisture, becoming again invisible.

Cobalt nitrate, $Co(NO_3)_2$, is one of the most common of the cobalt salts. It crystallizes with six molecules of water, forming beautifully red prisms.

Cobalt sulphate, $CoSO_4.7\,H_2O$, is a beautifully crystallized compound, and like so many other sulphates contains seven molecules of water of crystallization. It is isomorphous with ferrous sulphate.

Cobalt sulphide, CoS, is formed when ammonium sulphide is added to a solution of a cobaltous salt. When once formed cobalt sulphide does not dissolve in dilute acids, and this fact is made use of in separating it from other sulphides of the same group. Cobalt sulphide, however, is not precipitated from a solution of a neutral cobalt salt, unless some method is adopted to remove the free hydrogen ions which would be formed as the result of the reaction. This is effected by adding to the solution sodium acetate, when acetic acid is formed, and this is practically undissociated.

Cobalt forms *blue silicates.* When a cobalt salt is added to colorless glass and the mass fused, the resulting glass is deep blue in color. Cobalt glass is finely powdered and used as a pigment under the name of *smalt.* Cobalt glass cuts off the yellow rays of light, and it will be remembered that it is used for this purpose in qualitative analysis to detect the presence of potassium when sodium is present.

Cobalt also colors the microcosmic bead, or the borax bead, deep blue when heated in the flame of the blowpipe. This reaction is made use of to detect cobalt in blowpipe analysis.

Double Cyanides of Cobalt. — Cobalt forms two double cyanides, which are strictly analogous to the two compounds of iron. Where cobaltous cyanide is dissolved in potassium cyanide the two

combine and form potassium cobaltous cyanide, $K_4Co(CN)_6$. This is the analogue of potassium ferrocyanide, and dissociates into $\overset{+}{K}$, $\overset{+}{K}$, $\overset{+}{K}$, $\overset{+}{K}$, $Co(\overset{----}{C}N)_6$. The anion which contains the cobalt and six cyanogen groups is quadrivalent, like the ferrocyanogen ion.

When a solution of this compound is boiled in the presence of the oxygen of the air, the compound is oxidized to potassium cobalticyanide, $K_3Co(CN)_6$, which is analogous to potassium ferricyanide. In the presence of water this dissociates into $\overset{+}{K}$, $\overset{+}{K}$, $\overset{+}{K}$, $Co(\overset{---}{C}N)_6$, the cobalticyanogen ion being trivalent. The acid $H_3Co(CN)_6$ is well-known. From neither the cobaltocyanogen nor the cobalticyanogen ion do the ordinary precipitants of cobalt throw down the cobalt. The cobalt in these ions, like the iron in the corresponding ferro- and ferricyanogen ions, does not have the ordinary properties of cobalt.

Double Nitrite of Cobalt. — Cobalt forms a double nitrite with potassium, having the composition $K_3Co(NO_2)_6$. This is obviously the salt of the acid $H_3Co(NO_2)_6$, which, however, has never been isolated. It is formed by adding potassium nitrite to a solution of a cobalt salt. The difficultly soluble potassium salt is thus precipitated as a yellow powder. The corresponding sodium salt $Na_3Co(NO_2)_6$ is readily soluble in water.

Action of Ammonia on Solutions of Cobalt Salts. — When solutions of cobalt salts are treated with ammonia and exposed to the action of the air, a number of complex compounds are formed. These have been studied extensively, and the composition of a number of them established. Thus, compounds of the composition $[Co(NH_3)_4A'_2]A$ (where A is an anion, $\overline{Cl}$, $\overline{NO_3}$, etc., and A′ an acid-forming atom or group), etc., are known as *praseo* compounds. Another series of compounds are known having the composition $[Co(NH_3)_5A']A_2$, and are termed *purpureo* compounds, while still another series exists, having the composition $[Co(NH_3)_6]A_3$, and are known as the *luteo* compounds.

NICKEL (At. Wt. = 58.7)

An element which resembles cobalt in many respects is nickel. It occurs in nature chiefly in combination with arsenic, NiAs, as *niccolite*, and with arsenic and sulphur, NiAsS, as *gersdorffite*. The silicate occurs in abundance and is known as *garnierite*.

Nickel is prepared by reducing the oxide with carbon at a high temperature, and by reducing the oxide in a stream of hydrogen.

Nickel is light in color, with a yellowish cast. Although hard, it is malleable. It melts at about the same temperature as iron. It is

oxidized in the air with difficulty, but is dissolved by hydrochloric and sulphuric acids, and especially by nitric acid.

On account of its resistance to oxidation, nickel is extensively used to cover metals which are more readily oxidized, such as iron, etc. The nickel is deposited upon the iron electrolytically. The iron object is made the cathode of a suitable electric current, and this is immersed in a solution of a nickel salt, the double sulphate with ammonium being frequently used. The anode is of nickel, and supplies as much nickel to the bath as is deposited on the cathode. The nickel ions give up their charges to the cathode, and are deposited in the form of metal upon the cathode. This method of covering one metal with another is known as *electro-plating.*

Nickel forms valuable alloys with a number of the metals. *German silver* is an alloy of nickel with zinc and copper. Alloys of nickel and copper are used as coins; our so-called "nickel" containing 75 per cent copper and 25 per cent nickel.

Compounds of Nickel. — While there are a few compounds known in which nickel plays the rôle of a trivalent element, it is almost always present as the bivalent ion $\overset{++}{Ni}$. The *oxide* of nickel, NiO, is formed as a black powder when the hydroxide is heated in a limited supply of air. When there is an abundant supply of oxygen the *sesquioxide,* Ni_2O_3, is formed.

The green *hydroxide,* $Ni(OH)_2$, is formed when a solution of a nickel salt is treated with a solution of a hydroxide: —

$$NiCl_2 + 2\,KOH = 2\,KCl + Ni(OH)_2.$$

When the nickelous hydroxide is oxidized with chlorine, *nickelic* hydroxide, $Ni(OH)_3$, is formed. The *chloride* of nickel is formed by heating the metal in a current of chlorine. It crystallizes with nine molecules of water of crystallization — $NiCl_2 \cdot 9\,H_2O$.

When the oxide of nickel or the metal is dissolved in dilute sulphuric acid, the beautifully green sulphate crystallizes from the solution. This has the composition $NiSO_4 \cdot 7\,H_2O$, and readily forms double sulphates with the sulphates of the alkalies.

A remarkable compound of nickel is the one formed with carbon monoxide. When nickel and carbon monoxide remain in contact at 30°, they combine and form a liquid compound which has the composition $Ni(CO)_4$ and is known as *nickel carbonyl,* or *nickel tetracarbonyl.* Nickel carbonyl boils at 43° and solidifies at $-25°$. At a temperature somewhat above its boiling-point, nickel tetracarbonyl decomposes into nickel and carbon monoxide. This method has been used for purifying nickel, but has the disadvantage that the

carbon monoxide set free decomposes in part into carbon dioxide and carbon.

The *cyanide* of nickel is formed when potassium cyanide is added to a solution of a nickel salt:—

$$2\,KCN + NiSO_4 = K_2SO_4 + Ni(CN)_2.$$

The greenish cyanide which is precipitated readily dissolves in an excess of potassium cyanide, forming the *double cyanide* $K_2Ni(CN)_4$. When potassium nickelous cyanide is treated with an acid, in all probability the acid $H_2Ni(CN)_4$ is formed, but this is decomposed at once into hydrocyanic acid and nickel cyanide.

With potassium nitrite nickel forms the double nitrite, $K_4Ni(NO_2)_6$.

CHAPTER XXXV

MANGANESE (At. Wt. = 55.0)

We now come to an element which probably forms as large a variety of compounds as any element known. This is due to the many degrees of valence which manganese can manifest. On the whole, the element shows many analogies to iron, and undoubtedly belongs in the iron group. While there are certain analogies between manganese and chlorine, they are not very striking. Indeed, far less striking than the differences, and it must be regarded as a weakness in the Periodic System that manganese falls in the same group with the halogens.

Occurrence, Preparation, and Properties of Manganese. — Manganese occurs in nature in small quantities in the free condition, but usually as one of its oxides. The chief source of manganese is the oxide MnO_2, which is the mineral *pyrolusite.* Other manganese minerals are *hausmannite,* Mn_3O_4, *braunite,* Mn_2O_3, and *rhodocroisite,* $MnCO_3$.

Manganese is prepared by heating the oxides with carbon in an electric furnace, also by electrolysis of the fused chloride, but more conveniently by mixing the oxide with finely divided aluminium and igniting the mixture. This is one of Goldschmidt's mixtures, the aluminium taking the oxygen, setting free the manganese.

Manganese has but little commercial value, since it is so readily attacked by chemical reagents. It is oxidized in the air, decomposes water even at ordinary temperatures, and is readily attacked by acids.

Some of the *alloys of manganese* are of value. The alloy with iron known as *spiegel iron,* has already been referred to. The alloy with copper containing some zinc is known as *manganese bronze,* and is quite valuable.

Oxides of Manganese. — Manganese forms no less than seven compounds with oxygen. The one containing the smallest amount of oxygen is manganous oxide, MnO. This is formed by reducing the higher oxides in a stream of hydrogen, and by heating manganous hydroxide. Manganese sesquioxide, Mn_2O_3, occurs in nature as *braunite.* Manganous-manganic oxide, Mn_3O_4, is formed when the

other oxides of manganese are heated in the air. Manganese dioxide, MnO_2, occurs in nature as *pyrolusite,* and is the most important ore of manganese. There exists a trioxide of manganese, MnO_3, and also a septoxide, Mn_2O_7. The latter is formed by treating potassium permanganate with sulphuric acid: —

$$2\,KMnO_4 + H_2SO_4 = K_2SO_4 + H_2O + Mn_2O_7.$$

There also exists a tetroxide of manganese — MnO_4. Arranging these oxides in the order of increasing amount of oxygen, we have: —

		MnO_3
MnO	Mn_2O_3	Mn_2O_7
Mn_3O_4	MnO_2	MnO_4.

Hydroxides of Manganese. — *Manganous hydroxide* is precipitated as a white powder when an alkali is added to a manganous salt: —

$$MnCl_2 + 2\,NaOH = 2\,NaCl + Mn(OH)_2.$$

Manganous hydroxide readily takes up oxygen in the presence of alkalies and passes over into the dark-brown *manganic hydroxide,* $Mn(OH)_3$. Manganic hydroxide minus water, $HMnO_2$, occurs in nature as *manganite.*

The hydroxide $Mn(OH)_4$ can be prepared by treating a manganous salt with an alkali in the presence of oxidizing agents. This hydroxide minus water is *manganous acid,* H_2MnO_3, which forms a series of salts known as the *manganites.*

The partial anhydride of the supposed hydroxide $Mn(OH)_6$, which can be regarded as formed from that substance by loss of two molecules of water — H_2MnO_4 — is *manganic acid.* This acid is unstable and does not exist in the free condition. Salts of this acid, or the *manganates,* are well known.

One other hydroxyl compound of manganese merits special consideration. This is *permanganic acid.* It has the composition $HMnO_4$, and may be regarded as the partial anhydride of the hydroxide $Mn(OH)_7$: —

$$Mn(OH)_7 = 3\,H_2O + HMnO_4.$$

Permanganic acid is quite stable in aqueous solution, and can be prepared by dissolving manganese septoxide in water, but far more conveniently by electrolyzing the potassium salt, as we shall see. By this method permanganic acid can readily be prepared in any quantity desired.

Manganous Salts. — The manganous ion, $\overset{++}{Mn}$, combines with the anions of acids, forming salts which are usually beautifully crystal-

lized compounds. *Manganous chloride,* $MnCl_2.4\,H_2O$, is formed by the action of hydrochloric acid on manganese dioxide: —

$$MnO_2 + 4\,HCl = 2\,H_2O + Cl_2 + MnCl_2.$$

When manganous chloride is treated with lime-water, manganous hydroxide is formed: —

$$MnCl_2 + Ca(OH)_2 = CaCl_2 + Mn(OH)_2.$$

When manganous hydroxide is treated with lime and allowed to stand exposed to the air, it undergoes oxidation and forms the calcium salt of the acid H_2MnO_3, which is $Mn(OH)_4 - H_2O$: —

$$2\,Mn(OH)_2 + O_2 + 2\,CaO = 2\,H_2O + 2\,CaMnO_3.$$

In the *Weldon process* for making chlorine, the above transformations are effected in order that the manganese chloride which is formed may not be lost. When *calcium manganite* is treated with hydrochloric acid, chlorine is set free, just as when the original manganese dioxide was treated with hydrochloric acid: —

$$CaMnO_3 + 6\,HCl = MnCl_2 + CaCl_2 + 3\,H_2O + Cl_2.$$

Manganous sulphide, MnS, occurs in nature as *manganese blende.* It is prepared by passing the vapors of carbon disulphide over heated manganite. It is dark in color as it occurs in nature. It is soluble in dilute acids, and cannot, therefore, be precipitated from solutions of manganous salts by hydrogen sulphide. When ammonium sulphide is added to a solution of a manganous salt a pinkish precipitate is formed, which is a hydrate of manganous sulphide. When this is allowed to stand it loses water and forms green manganous sulphide. When ammonium sulphide is added to a hot, concentrated solution of a manganous salt, the anhydrous, green sulphide is thrown down at once.

Manganous sulphate, $MnSO_4$, is formed by dissolving the oxides of manganese in hot, concentrated, sulphuric acid. It does not matter which oxide is used, the product is the manganous salt. This means that under these conditions the higher oxides must lose oxygen when boiled with concentrated sulphuric acid, and such is the fact. The salt exists in a number of crystal forms, depending upon the conditions of its formation. When the temperature of the solution from which the salt crystallizes is 0° or below, a salt with seven molecules of water separates, $MnSO_4.7\,H_2O$. This modification is analogous to ferrous sulphate. The modification with five molecules of water, $MnSO_4.5\,H_2O$, crystallizes from a solution between 15° and 20°. This is analogous to copper sulphate. At a still

higher temperature, 20° to 30°, the salt $MnSO_4 . 4\,H_2O$ is formed; while at much higher temperatures, extending even above 200°, the salt $MnSO_4 . H_2O$ is stable.

Manganous carbonate, $MnCO_3$, occurs in nature under the name of *manganese spar*, and is formed when a manganous salt is treated with a soluble carbonate. When heated in contact with the air, it forms the compound Mn_3O_4, like most manganese compounds.

Manganic Compounds. — The manganic ion, $\overset{+++}{Mn}$, can unite with the anions of acids and form salts. The manganic salts are, however, not as numerous as the manganous, and in general not as stable, being strongly hydrolyzed by water. A few of these will, however, be considered. The oxide, Mn_2O_3, the hydroxide, $Mn(OH)_3$, and the partial anhydride, $HMnO_2$, have already been referred to. When manganic hydroxide is treated with hydrochloric acid, there is reason to believe that *manganic chloride*, $MnCl_3$, is formed. This cannot be isolated, since it decomposes spontaneously on standing into chlorine and manganous chloride.

Manganic sulphate, $Mn_2(SO_4)_3$, is formed when manganese dioxide, MnO_2, or manganous-manganic oxide, is dissolved in slightly warmed sulphuric acid. If the acid is hot, oxygen escapes and manganous sulphate is formed, as we have seen. The dark-green manganic sulphate is comparatively unstable, easily losing oxygen and forming manganous sulphate. It is, therefore, an excellent oxidizing agent. It combines with the alkaline sulphates, forming manganese alums of the general composition, $MMn(SO_4)_2 . 12\,H_2O$.

Tetravalent Manganese. — A few compounds are known in which tetravalent manganese apparently exists. This is the case with the oxide, MnO_2, the hydroxides, $Mn(OH)_4$, H_2MnO_3, the supposed chloride, $MnCl_4$, and the sulphide, MnS_2. The most important of these substances is manganese dioxide, which, as we have seen, formerly found extensive application in the preparation of chlorine, and to-day is largely used in the arts as an oxidizing agent.

It is also used in the construction of one of the most efficient forms of primary cells, the *Leclanché cell.* The action of this cell, which consists of carbon and manganese dioxide as one pole, and zinc as the other pole, ammonium chloride being the electrolyte, depends largely upon the transformation of tetravalent manganese, $\overset{++++}{Mn}$, into manganese of lower valence.

Valence and Properties of Manganese. — It should be noted that as the valence of manganese increases, its basic nature rapidly diminishes. Bivalent manganese is distinctly basic, forming stable salts

with the anions of acids. Trivalent manganese is very weakly basic, its salts being strongly hydrolyzed by water. Tetravalent manganese is scarcely basic at all, its compound with such a strong acid as hydrochloric being so unstable that its very existence is doubtful.

When we pass to manganese with higher valence, not only has all the basic nature been lost, but we find acid properties beginning to manifest themselves, and the highest oxidation product of manganese is a strong acid. These acid compounds of manganese we shall now study.

Manganous Acid, H_2MnO_3, can be regarded as formed from the hydroxide, $Mn(OH)_4$, by loss of one molecule of water. Salts of the above compound are known. Calcium manganite, $CaMnO_3$, is formed, as we have seen, by the action of oxygen on a mixture of manganous hydroxide and lime. It is the so-called *Weldon mud*, obtained in the preparation of chlorine by the Weldon process, using manganese dioxide and hydrochloric acid. This compound is not very stable, easily losing oxygen and passing into the manganous condition.

Manganic Acid, H_2MnO_4. — We have now studied compounds of manganese in which this element has appeared in the capacity of a bivalent, trivalent, and quadrivalent ion. Pentavalent manganese is not known, but hexavalent manganese is well known, manifesting itself in salts of the compound manganic acid, the analogue of sulphuric acid. These are formed, as we would expect, by strongly oxidizing manganese in the presence of bases. *Potassium manganate*, K_2MnO_4, is formed by fusing potassium hydroxide with manganese dioxide in the presence of the oxygen of the air, or better, with an oxidizing agent such as potassium chlorate. The manganese is oxidized from the tetravalent to the hexavalent condition, the potassium chlorate being reduced to potassium chloride: —

$$3\,MnO_2 + KClO_3 + 6\,KOH = KCl + 3\,H_2O + 3\,K_2MnO_4.$$

This mass forms a green solution, from which green crystals of potassium manganate, K_2MnO_4, separate. This compound is stable only in alkaline solutions. When brought into the presence of the air or an acid it decomposes, owing to the instability of manganic acid itself. Indeed, the acid is so unstable that it has never been isolated. When potassium manganate is treated with an acid the following reaction takes place: —

$$3\,K_2MnO_4 + 6\,HCl = 6\,KCl + 2\,HMnO_4 + MnO_2 + 2\,H_2O.$$

Instead of obtaining manganic acid this breaks down into manganese dioxide and permanganic acid. This same transformation is effected

by carbon dioxide and, consequently, takes place slowly when a manganate is exposed to the air: —

$$3\,K_2MnO_4 + 2\,CO_2 = MnO_2 + 2\,K_2CO_3 + 2\,KMnO_4.$$

The change of color from the green manganate, through blue and purple to the purplish-red permanganate, is very striking. This was early observed and termed *mineral chameleon.*

Permanganic Acid, $HMnO_4$. — The highest oxidation product of manganese containing hydrogen and oxygen is permanganic acid, $HMnO_4$, the analogue of perchloric acid and persulphuric acid. One method of preparing the acid which we have just studied consists in the action of acids on potassium manganate. Another method which has already been referred to consists in the electrolysis of the potassium salt of this acid. This method, which was devised by Morse, is carried out as follows: Two unglazed porcelain cups containing the one water to which a little alkali is added, and the other water to which a little permanganic acid is added if available to make the water conducting, are immersed in a beaker containing a solution of potassium permanganate. The platinum electrodes are inserted the one in each cup, the cathode in the cup containing the alkali. The current is passed, when the potassium ions move toward the cathode, give up their charge, decompose water, and liberate hydrogen. The alkali formed around the cathode is easily siphoned off from time to time. The permanganic ions, $\bar{MnO_4}$, move to the anode, decompose water forming permanganic acid, and liberate oxygen. The permanganic acid collects in the cup around the anode, and after the current has been passed for a sufficient time can be obtained in perfectly pure condition and in any quantity desired. This method of preparing permanganic acid so far surpasses all others that they are only of historical interest. Permanganic acid is a very strong acid as is shown by its large conductivities.

v	μ_v	a
16	352 3	93.4 %
128	375.0	99.3
512	376.6	99.8
1024	377.3	100.0

Potassium permanganate, $KMnO_4$, is readily obtained by passing carbon dioxide through a solution of potassium manganate, as

already described. Its solution has exactly the same color as permanganic acid, — purplish-red. It crystallizes in beautiful purplish-red crystals, which are not very soluble in water, one part of salt requiring about sixteen parts of water to dissolve it at ordinary temperatures.

Potassium permanganate is characterized chiefly by its oxidizing power. When its aqueous solution is treated with an alkali in the presence of a reducing agent, it breaks down as follows: —

$$2\,KMnO_4 + \text{alkali} + 5\,H_2O = 2\,KOH + 2\,Mn(OH)_4 + \text{alkali}, + 3\,O,$$

two molecules of the salt giving three oxygen atoms.

In the presence of an acid, however, the reduction goes much farther, the manganese being reduced to the manganous condition: —

$$2\,KMnO_4 + 3\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 3\,H_2O + 5\,O,$$

two molecules of the permanganate yielding five atoms of oxygen.

The oxidizing action of the permanganates is shown especially by those permanganates which are very soluble in water. Calcium and strontium permanganates are extremely soluble in water, one part of water dissolving 2.9 parts of strontium permanganate and 3.3 parts of calcium permanganate. Concentrated solutions of these salts oxidize organic compounds with the greatest energy. When a drop of the solution of the permanganate is allowed to fall into oil of turpentine or glycerine, the oxidation takes place almost with explosive violence.

On account of its oxidizing action potassium permanganate is used extensively in analytical chemistry. It always yields a definite amount of oxygen in alkaline solution and a definite amount in acid solution, and its oxidizing power is therefore known. It is only necessary to know the strength of the solution of the permanganate and the amount used, in order to know the amount of oxidation which will be effected.

As an example of the uses of potassium permanganate in analytical chemistry, take its action on oxalic acid. This substance is oxidized to carbon dioxide and water by the permanganate in acid solution. Knowing the strength of the permanganate solution, and the amount employed to just oxidize all of the oxalic acid, we can calculate at once the strength of the solution of oxalic acid. The end of this reaction is determined by the appearance

of the color of the permanganate as soon as all of the oxalic acid is used up.

Color of Permanganates. — The color of the solutions of the permanganates is of special interest in connection with the theory of electrolytic dissociation. The permanganates are compounds of the metal cations with the anion, $\mathrm{M\bar{n}O_4}$. If we select cations which are colorless, the color of these permanganates is due entirely to the permanganic ion, $\mathrm{M\bar{n}O_4}$. They should all, therefore, have *exactly the same color.*

This interesting conclusion from the theory of electrolytic dissociation has been tested experimentally by Ostwald. He prepared solutions of a number of salts of permanganic acid with such colorless cations as potassium, sodium, ammonium, lithium, barium, magnesium, aluminium, zinc, cadmium, etc., and then studied their absorption spectra, or the wave-lengths of lights which would be cut off when white light was passed through their solutions. The absorption bands were both measured and photographed by Ostwald. These salts show five absorption bands in the yellow and green, and four of these were measured by Ostwald for thirteen salts of permanganic acid.

The results of Ostwald's measurements are given in the following table: —

PERMANGANATES. ABSORPTION BANDS

	I	II	III	IV
Hydrogen	2601 ± 0.5	2698 ± 0.8	2804 ± 0.7	2913 ± 1.7
Potassium	2600 ± 1.3	2697 ± 0.1	2803 ± 0.9	2913 ± 1.1
Sodium	2602 ± 1.2	2698 ± 0.8	2803 ± 0.7	2913 ± 0.8
Ammonium	2601 ± 1.3	2698 ± 1.4	2802 ± 0.1	2913 ± 0.1
Lithium	2602 ± 0.2	2700 ± 0.2	2804 ± 0.8	2914 ± 1.7
Barium	2600 ± 0.9	2699 ± 0.8	2804 ± 0.6	2914 ± 1.3
Magnesium	2602 ± 0.8	2700 ± 0.6	2802 ± 0.7	2912 ± 1.8
Aluminium	2603 ± 0.4	2699 ± 0.9	2804 ± 0.9	2914 ± 0.7
Zinc	2602 ± 0.5	2699 ± 0.7	2802 ± 1.2	2912 ± 1.1
Cobalt	2601 ± 0.2	2698 ± 0.1	2803 ± 0.9	2912 ± 1.7
Nickel	2603 ± 0.5	2700 ± 0.7	2804 ± 0.7	2913 ± 1.8
Cadmium	2600 ± 0.1	2700 ± 0.2	2803 ± 0.8	2913 ± 1.4
Copper	2602 ± 1.2	2699 ± 0.1	2803 ± 0.9	2913 ± 0.8

The spectra of ten of these salts were photographed, the one directly over the other, and the results are given in the accompanying figure (Fig. 42). The agreement between the position and character of the bands is so striking, that there is no room for doubt that these salts show the same absorption bands.

Ostwald concluded from these results that the absorption spectra

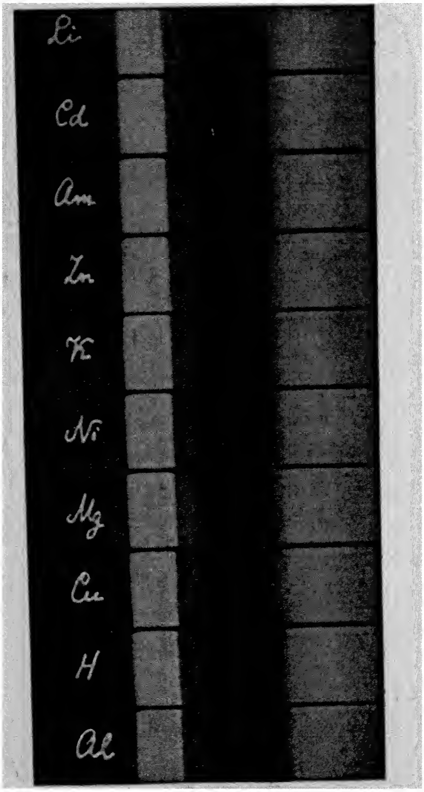


FIG. 42.

of all the thirteen salts are exactly the same to within the limit of error of measurement.

This is one of the many beautiful confirmations of the conclusions led to by the theory of electrolytic dissociation.

One other element of the iron group is of special importance on account of the number and variety of the compounds which it forms, and the importance of some of the substances. This element is chromium.

CHAPTER XXXVI

CHROMIUM (At. Wt. = 52.1)

Chromium forms a number of series of compounds, and many of these are closely related to iron and manganese. It occurs in nature largely as chrome iron ore, which is *iron chromite*, having the composition $Fe(CrO_2)_2$. It also occurs as the lead salt of chromic acid, $PbCrO_4$, or *crocoisite*.

Chromium is readily prepared by heating a mixture of chromic oxide and carbon in an electric furnace. The lime which is added decomposes the carbides of chromium, forming calcium carbide and metallic chromium. Chromium is prepared most conveniently by heating the oxide with finely divided aluminium, according to the method of Goldschmidt.

Chromium is light in color, with a high lustre, and is not attacked by oxygen at ordinary temperatures. It is very hard and does not melt until a temperature of 3000° is reached. It dissolves in hydrochloric and sulphuric acids, but not in nitric acid. When treated with acids it does not always dissolve continuously, but frequently shows *periodical* or *rhythmical* phenomena. It dissolves, then becomes passive, dissolves again, is again passive, and so on. This phenomenon, however, is not manifested alone by chromium.

Chromium forms alloys with a number of the metals, such as aluminium and iron, and amalgams with mercury; but these compounds are without special interest.

Oxides of Chromium.—Chromium, like manganese, forms a number of oxides. *Chromous oxide*, CrO, is formed by reducing the higher oxides. It is a green powder, insoluble in water and most acids. *Chromic oxide* or *chromium sesquioxide*, Cr_2O_3, is formed by heating the trioxide, or by heating chromic hydroxide. It is a green powder, and when highly heated difficultly soluble in acids. It imparts a green color to glass. It dissolves in alkalies, forming *chromites*, $MCrO_2$. *Chromium trioxide*, CrO_3, is formed by adding concentrated sulphuric acid to potassium dichromate in very concentrated solution:

$$K_2Cr_2O_7 + H_2SO_4 = K_2SO_4 + H_2O + 2\,CrO_3.$$

It is a dark-red, beautifully crystalline substance, characterized by its tremendous oxidizing power. When brought in contact with organic compounds these are oxidized or burned up, as we say, and chromium trioxide is reduced to a lower oxide of chromium.

A still higher oxide of chromium, CrO_4, is supposed to exist in solution, but has not been isolated.

Hydroxides of Chromium. — Just as chromium can form a number of oxides, just so it can form a number of hydroxides. *Chromous hydroxide*, $Cr(OH)_2$, is formed when a chromous salt is treated with a strong base: —

$$CrCl_2 + 2\,KOH = 2\,KCl + Cr(OH)_2.$$

This is a yellow solid which quickly undergoes oxidation on the air. *Chromic hydroxide*, $Cr(OH)_3$, is formed by the addition of ammonia or ammonium sulphide to a chromic salt: —

$$CrCl_3 + 3\,NH_4OH = 3\,NH_4Cl + Cr(OH)_3,$$
$$2\,CrCl_3 + 3\,(NH_4)_2S + 6\,H_2O = 3\,H_2S + 2\,Cr(OH)_3 + 6\,NH_4Cl.$$

As ordinarily formed it contains two molecules of water, but this can be easily removed by drying in a vacuum. It readily loses water, forming the compound $HCrO_2$, which is a weak acid.

The hydroxide H_2CrO_4, which is $Cr(OH)_6 - 2\,H_2O$, is not known in the free condition. This is *chromic acid*, and its salts are stable compounds. When it is set free from its salts by addition of an acid, it loses water at once, forming the anhydride CrO_3. Salts of a *perchromic acid*, $HCrO_4$, have also been described.

Valence and Properties of Chromium Ions. — It is obvious, from the composition of the oxides and hydroxides of chromium, that this element can exist in various conditions of valence. Bivalent chromium ions, $\overset{++}{Cr}$, are distinctly basic, as is shown by the hydroxide. The bivalent ions, however, readily pass into trivalent ions, $\overset{+++}{Cr}$, which are very weakly basic towards strong acids, and are acidic towards certain bases. This is strictly analogous to the ions of iron and manganese. Those of lower valence, or with the smaller electrical charge, are basic; but as the valence increases or as the amount of electrical energy which they carry increases, the basic property becomes less and less, and acidic properties begin to manifest themselves. When the valence of the chromium ion reaches six, as in the compound H_2CrO_4, we have a very strong acid, chromic acid, and, similarly, when it reaches seven in *perchromic acid*, $HCrO_4$. This is analogous to iron, and especially to manganese, where the sexavalent

ion is acidic as in manganic acid, and the septivalent ion strongly acidic as in permanganic acid. We shall now study somewhat in detail these several classes of chromium compounds.

Chromous Salts. — The chromous ion, Cr^{++}, combines with the anions of acids, forming salts. These, however, readily absorb oxygen and pass over into chromic compounds. The chromous compounds must, therefore, be protected from contact with the air in order to preserve them pure. They can be prepared by reducing the chromic compounds with zinc and sulphuric acid; also by the action of acids on chromium. The yellow hydroxide has already been referred to.

Chromous chloride, $CrCl_2$, is obtained by reducing chromic chloride with zinc and sulphuric acid, or by heating chromic chloride in a current of hydrogen. Its solution is blue, since the chromous ion, Cr^{++}, is blue in color.

Chromous acetate, $(CH_3COO)_2Cr$, is formed when sodium acetate is added to a solution of a chromous salt. It is not readily soluble and is, therefore, precipitated. It is dark red, crystalline, and fairly stable, and can be used in preparing other chromous salts. Thus, when chromous acetate is treated with concentrated hydrochloric acid, the following reaction takes place: —

$$Cr(CH_3COO)_2 + 2\,HCl = 2\,CH_3COOH + CrCl_2.$$

Chromous chloride not being very soluble in hydrochloric acid, can be obtained from this solution in crystals, which are blue in color.

Chromic Salts. — Chromous chromium, Cr^{++}, readily passes, as we have seen, into chromic chromium, Cr^{+++}. The chromic ion, while not very strongly basic, unites with the anions of acids forming salts.

Chromic Chloride, $CrCl_3$, is obtained in the anhydrous condition by passing chlorine over a heated mixture of chromic oxide and carbon. It sublimes and crystallizes in plates of a violet color. Chromic chloride dissolves very slowly in water unless a chromous salt is present, when it readily dissolves, giving a green solution. It crystallizes from the aqueous solution with six molecules of water, $CrCl_3 . 6\,H_2O$. When the salt with water of crystallization is heated, it decomposes into hydrochloric acid and chromic oxide. This is analogous to the conduct of most chlorides of weak bases, which contain water of crystallization.

When the hydrated chloride is heated in an atmosphere of hydrochloric acid the water is given off and the anhydrous salt, which is violet in color, is formed. This violet salt dissolves in water form-

ing a green solution. If, however, the violet salt is sublimed it recrystallizes in violet crystals, and these are practically insoluble in water. It is, thus, obvious that there are two compounds, one green and one violet. Both have been isolated.

From the green solution silver nitrate precipitates only two-thirds of the chlorine. When the green solution is allowed to stand it becomes violet, and then practically all of the chlorine can be precipitated by silver nitrate. In the violet solution we must have, then, the ions, $\overset{+++}{Cr}$, $\overset{-}{Cl}$, $\overset{-}{Cl}$, $\overset{-}{Cl}$, since silver is a reagent only for chlorine ions. In the green solution one-third of the chlorine is not present as such in the ionic condition, but must be united to the chromium forming part of the cation. The green solution must dissociate thus, $\overset{++}{CrCl}$, $\overset{-}{Cl}$, $\overset{-}{Cl}$. The vapor-density at 1200° corresponds to the simple molecule $CrCl_3$.

Chromic Sulphate, $Cr_2(SO_4)_3.15\,H_2O$, is formed by dissolving chromic hydroxide in concentrated sulphuric acid: —

$$2\,Cr(OH)_3 + 3\,H_2SO_4 = 6\,H_2O + Cr_2(SO_4)_3.$$

These crystals are violet in color and form a violet-colored solution. The salt $Cr_2(SO_4)_3.9\,H_2O$ can also be obtained from aqueous solution. If the aqueous solution is boiled it becomes green, but changes back slowly on cooling to violet. From the violet solution all of the sulphuric acid is precipitated by barium ions. It must, therefore, contain the ions, $\overset{+++}{Cr}$, $\overset{+++}{Cr}$, $\overset{=}{SO_4}$, $\overset{=}{SO_4}$, $\overset{=}{SO_4}$.

From the green solution, however, only one-third of the sulphuric acid is precipitated by barium ions. Therefore, two out of every three of the sulphuric ions, SO_4, are in combination with the chromium, forming part of the cation.

It has been shown that when the violet modification of the sulphate passes into the green one molecule of sulphuric acid separates from every two molecules of chromic sulphate. This reaction can be represented as follows: —

$$2\,Cr_2(SO_4)_3 + H_2O = H_2SO_4 + Cr_4(SO_4)_4OSO_4.$$

The complex green substance $Cr_4(SO_4)_4OSO_4$ dissociates into $\overset{++}{Cr_4(SO_4)_4O}$ and $\overset{=}{SO_4}$. It is the sulphuric ion $\overset{=}{SO_4}$ together with the ion from the free sulphuric acid which is precipitated by barium ions.

When a mixture of chromic sulphate and sulphuric acid is heated, the resulting solution gives no precipitate with barium ions, and shows none of the characteristics of the chromic ion, $\overset{+++}{Cr}$. The

hydrogen ions of the sulphuric acid, however, give normal reactions. These facts show that the chromic ions, $\overset{+++}{Cr}$, and sulphuric ions, $\overset{=}{SO_4}$, are combined, forming complexes, which are not dissociated by water into the simple ions.

Chromic sulphate, like aluminium sulphate and ferric sulphate, combines with the sulphates of the alkalies forming double sulphates or alums. Of the *chromium alums*, the potassium salt, $KCr(SO_4)_2 . 12\,H_2O$, is the best known. The double sulphates with chromium manifest the same general behavior as the simple chromium sulphate. The violet solutions become green when heated, and the green solutions have very different properties from the violet. They become violet on standing, and from the violet solutions the alums crystallize again.

Chromites. — The hydroxide, $Cr(OH)_3$, is a weak base, forming salts, as we have seen. This substance dissolves in strong bases showing its acid nature. It loses water and forms the compound $HCrO_2$, which is chromous acid. There are a number of salts of this compound known, and these are called chromites. Chromite itself, which occurs in nature in abundance, is the ferrous salt of chromous acid, $Fe(CrO_2)_2$.

Chromic Acid, H_2CrO_4. — In composition this acid resembles sulphuric acid, manganic acid, and the like. It may be looked upon as the partial anhydride of the hydroxide $Cr(OH)_6$: —

$$Cr(OH)_6 = 2\,H_2O + H_2CrO_4.$$

The compound H_2CrO_4 is, however, not known. When its salts are treated with sulphuric acid the anhydride CrO_3 is obtained, which is chromic acid minus water: —

$$H_2CrO_4 - H_2O = CrO_3.$$

In this compound the chromium is obviously sexivalent, and with its high valence the strongly acid properties begin to come out. *Chromic acid can be prepared also by electrolysis by the method used by Morse in preparing permanganic acid.*

Chromates. — Salts of this acid are formed when ferrous chromite (*chromite*) is heated on the air in the presence of an alkali. The chromium is oxidized to the chromate, which is soluble, and the iron to ferric oxide which is insoluble in water. The mixture is treated with water, when the chromate dissolves. If caustic potash is used the resulting compound is *potassium chromate.* This is deep yellow in color, due to the color of the chromic acid ion, $\overset{=}{CrO_4}$. It forms crystals which are isomorphous with potassium sulphate.

Barium chromate, $BaCrO_4$, is formed when barium ions, $\overset{++}{Ba}$,

come in contact with chromic acid ions, $\overset{=}{CrO_4}$. It is bright yellow in color, and is used as a pigment (*yellow ultramarine*). *Lead chromate*, $PbCrO_4$, which is quite insoluble, is formed when lead ions $\overset{++}{Pb}$, come in contact with chromic acid ions, $\overset{=}{CrO_4}$. On account of its fine yellow color and stability it is used as a pigment, and is termed *chrome yellow*. The chromates are in general beautifully yellow substances, silver being an exception, forming a red chromate.

Dichromates. — When a chromate like potassium chromate is treated with an acid, the color of the solution changes from yellow to red. The reaction in the case of potassium chromate may be represented as follows: —

$$2\,K_2CrO_4 + H_2SO_4 = H_2O + K_2SO_4 + K_2Cr_2O_7.$$

Potassium dichromate, $K_2Cr_2O_7$, crystallizes from the solution in beautiful red crystals, which often grow to unusual size and are of unusual geometrical perfection. Potassium dichromate is a powerful oxidizing agent. It readily gives up oxygen, the chromium being reduced to the chromic condition. When sulphuric acid is used we have: —

$$2\,K_2Cr_2O_7 + 8\,H_2SO_4 = 8\,H_2O + 3\,O_2 + 4\,KCr(SO_4)_2.$$

Potassium chrome alum is formed.

When hydrochloric acid is added to potassium dichromate there are formed chromic chloride, potassium chloride, water, and instead of oxygen chlorine is liberated. This is one of the most convenient methods of preparing pure chlorine on a small scale.

When potassium dichromate is treated with caustic potash potassium chromate is formed: —

$$K_2Cr_2O_7 + 2\,KOH = 2\,K_2CrO_4 + H_2O.$$

This is made evident by the change in the color of the solution from red to yellow. It will be observed that the valence of the chromium in potassium dichromate is the same as in potassium chromate. The change from the former to the latter by the addition of an alkali, and the reverse change by the addition of an acid, therefore, involve neither oxidation nor reduction.

While the chromates of the heavy metals are in general very insoluble compounds, the dichromates are soluble. If potassium dichromate is added to a solution of a salt of a heavy metal the dichromate is not formed, but the chromate, since it is insoluble.

Thus, if potassium dichromate is added to lead nitrate we have: —

$$2\,Pb(NO_3)_2 + K_2Cr_2O_7 + H_2O = 2\,PbCrO_4 + 2\,KNO_3 + 2\,HNO_3.$$

There are many cases known which are similar to the above.

The Ions $\overset{=}{CrO_4}$ and $\overset{=}{Cr_2O_7}$. — We have seen that when a chromate is treated with an acid, *i.e.* with hydrogen ions, it forms the dichromate. This means that the chromic ions, $\overset{=}{CrO_4}$, pass over into dichromic ions, $\overset{=}{Cr_2O_7}$. The reaction is expressed thus: —

$$2\,\overset{=}{CrO_4} + \overset{+}{H} + \overset{+}{H} = H_2O + \overset{=}{Cr_2O_7}.$$

This reaction always takes place whenever hydrogen ions are present. It therefore takes place in the presence of pure water, since pure water is dissociated to a slight extent.

This is in accord with the facts: Chromium trioxide dissolved in water shows the red color of the $\overset{=}{Cr_2O_7}$ ions, and Ostwald has shown by purely physical chemical methods that the ions $\overset{=}{Cr_2O_7}$ exist in aqueous solutions of chromic acid.

When a dichromate is treated with an alkali it is transformed into a chromate, *i.e.* the ions $\overset{=}{Cr_2O_7}$ are transformed into $\overset{=}{CrO_4}$. This transformation is effected by hydroxyl ions: —

$$\overset{=}{Cr_2O_7} + \overset{-}{O}H + \overset{-}{O}H = H_2O + 2\,\overset{=}{CrO_4}.$$

The reciprocal transformations of chromates and dichromates are then only transformations of the ions $\overset{=}{CrO_4}$ and $\overset{=}{Cr_2O_7}$.

Chlorides of Chromic Acid. — When potassium dichromate is mixed with sodium chloride and sulphuric acid, and the mixture distilled, a dark-red liquid passes over which has the composition CrO_2Cl_2. This can be regarded as chromic acid in which the two hydroxyl groups are replaced by chlorine. From its analogy to sulphuryl chloride it is called *chromyl chloride.* It is readily decomposed by water, and easily gives up oxygen. The monochlor derivative of chromic acid, or *chlorchromic* acid, is not known in the free condition. The potassium salt, $KCrO_3Cl$, is prepared by boiling a solution of potassium dichromate with concentrated hydrochloric acid. From this solution the orange-red salt crystallizes.

Perchromic Acid is formed by treating chromic acid with such strong oxidizing agents as hydrogen dioxide. A solution of potassium dichromate and sulphuric acid treated with a few drops of hydrogen dioxide turns a beautiful blue color. This is supposed to be due to the formation of perchromic acid. The compound formed is not stable, since the blue color quickly disappears, oxygen being evolved. The compound, however, is more stable in ether, and when the above solution is shaken with ether this acquires the beautiful

blue color of perchromic acid, which persists for a considerable time. From the composition of the alkali salts this acid seems to have the composition $HCrO_5$.

Detection of Chromium. — Chromium is not precipitated from its salts by hydrogen sulphide. It is precipitated by ammonium sulphide not as chromium sulphide but as chromium hydroxide, as we have already seen. Chromium, therefore, belongs in the ammonium sulphide group.

CHAPTER XXXVII

MOLYBDENUM, TUNGSTEN, AND URANIUM

MOLYBDENUM (At. Wt. = 96.0)

Molybdenum is related to chromium in many respects, and it seems advisable to study it in this connection. It occurs chiefly as the sulphide, MoS_2, *molybdenite*, and as lead molybdate, $PbMoO_4$, *wulfenite*.

The sulphides are roasted and converted into the trioxide MoO_3. When the oxides are heated with carbon, or the oxides or chlorides heated in a current of hydrogen, the element is obtained.

Molybdenum is steel gray in color, and melts only at enormously high temperatures. It is not attacked by dilute sulphuric or hydrochloric acid, but readily dissolves in nitric acid. It combines with the oxygen of the air only at high temperatures.

The chemistry of molybdenum is complex, on account of the large variety of compounds which it forms. A few of these will be briefly considered.

Oxides of Molybdenum. — Oxygen and molybdenum form three compounds, Mo_2O_3, MoO_2, and MoO_3. The sesquioxide, Mo_2O_3, is weakly basic, the dioxide has neither acid nor basic properties, while the trioxide, MoO_3, is the anhydride of molybdic acid. The trioxide is formed when the sulphide is roasted. It is a white powder, practically insoluble in water.

Molybdic Acid, H_2MoO_4. — Molybdenum trioxide fused with an alkaline hydroxide forms salts. These are salts of the normal acid H_2MoO_4, or of polymolybdic acid derived from the normal acid by loss of water. When ammonium molybdate is treated with nitric acid, molybdic acid, $H_2MoO_4.H_2O$, is obtained in crystals.

Molybdic acid readily forms complexes by losing water and several molecules uniting. Thus: —

$$2\,H_2MoO_4 = H_2O + H_2Mo_2O_7,$$
$$3\,H_2MoO_4 = 2\,H_2O + H_2Mo_3O_{10}.$$

Salts of these polymolybdic acids are well known. Molybdenum trioxide forms complex acids by uniting with other acids. The best

known is the compound with phosphoric acid—*phosphomolybdic acid.*

Ammonium molybdate treated with nitric acid gives free molybdic acid: —

$$(NH_4)_2MoO_4 + 2\,HNO_3 = 2\,NH_4NO_3 + H_2MoO_4.$$

This dissolves in an excess of nitric acid. If phosphoric acid is added to this solution, the very difficultly soluble ammonium phosphomolybdate separates as a yellow precipitate. This has the composition $(NH_4)_3PO_4.12\,MoO_3.6\,H_2O$, and is the ammonium salt of phosphomolybdic acid, $H_3PO_4.12\,MoO_3.12\,H_2O$, which is obtained by dissolving ammonium phosphomolybdate in aqua regia and allowing the solution to evaporate. The free acid forms yellow crystals. This compound is very important, both in detecting and determining phosphoric acid quantitatively. The phosphoric acid is thrown down at first as the phosphomolybdate. This dissolves readily in an excess of ammonia, and from the ammoniacal solution the phosphoric acid can be precipitated by "magnesia mixture" as ammonium magnesium phosphate. This, when heated, forms the pyrophosphate, which can be readily weighed.

Compounds of Chlorine with Molybdenum. — Molybdenum forms an unusually large number of compounds with chlorine. *Molybdenum dichloride,* $MoCl_2$, is formed by heating the trichloride in a current of carbon dioxide. The *trichloride,* $MoCl_3$, is formed by reducing the pentachloride in a current of hydrogen. In appearance it resembles red phosphorus. The *tetrachloride,* $MoCl_4$, is also formed when the trichloride is heated. It is volatile. *Molybdenum pentachloride,* $MoCl_5$, is formed when molybdenum is heated in a current of chlorine. It boils at 268° and melts at 194°. The molecular weight, calculated from the vapor-density, corresponds to the formula $MoCl_5$. The compounds of chlorine with molybdenum are, then, $MoCl_2$, $MoCl_3$, $MoCl_4$, and $MoCl_5$. This is a very unusual series of substances.

Molybdenum also forms *oxychlorides.* Thus, we have MoO_2Cl_2, $Mo_2O_3Cl_6$, etc.

TUNGSTEN (At. Wt. = 184.0)

An element closely analogous to molybdenum is tungsten, which is represented by the symbol W (Wolfram). The analogy is to be found partly in the large variety of the compounds which the two elements form with chlorine, and the relations between the compositions of the two sets of chlorides.

Tungsten occurs in nature as salts of tungstic acid. Thus, we find calcium tungstate, $CaWO_4$, or *scheelite*, iron tungstate, $FeWO_4$, or *wolframite*, lead tungstate, $PbWO_4$, or *stolzite*, and manganese tungstate, $MnWO_4$, or *hübnerite*. Tungsten is prepared by reducing its trioxide with carbon or hydrogen, or far more conveniently by means of finely divided aluminium. This is one of the elements obtained by the Goldschmidt method.

The metal is sufficiently hard to scratch glass, and the compound with carbon is harder than pure tungsten. It has a very high specific gravity, 16.5. It is not attacked by the oxygen of the air, and only slowly by the common acids at ordinary temperatures. At higher temperatures it forms the trioxide. Tungsten forms alloys, especially with aluminium and steel. The presence of even a small amount of tungsten in steel increases its hardness very considerably, and tungsten steel has come into use for many purposes.

Chlorides of Tungsten. — Tungsten forms a number of chlorides, which, in general, correspond in composition to the chlorides of molybdenum. The trichloride of tungsten, however, is not known, while a hexachloride exists, and this has no counterpart among the chlorides of molybdenum.

The dichloride, WCl_2, is obtained as the lowest reduction product of the hexachloride in a current of hydrogen. The tetrachloride, WCl_4, is formed by heating the pentachloride in an indifferent gas. The pentachloride, WCl_5, is formed by distilling the hexachloride, which gradually loses chlorine when volatilized. The hexachloride, WCl_6, is formed by heating the metal in a current of chlorine.

Such a series of compounds of an element with chlorine finds few parallels in the whole field of chemistry. Molybdenum, as we have just seen, forms, however, four compounds with chlorine.

Tungsten also forms the oxychlorides $WOCl_4$ and WO_2Cl_2.

Tungstic Acid, H_2WO_4. — Tungsten forms a dioxide, WO_2, which, at elevated temperatures, readily takes up oxygen and forms tungsten trioxide, WO_3. This is the anhydride of tungstic acid. When a tungstate is treated with an acid at an elevated temperature, the anhydride WO_3 is formed. At lower temperatures tungstic acid, H_2WO_4, is thrown down.

As we have seen, tungsten occurs in nature mainly in the form of salts of this acid. When the oxide is dissolved in strong alkalies, the corresponding salt is formed — M_2WO_4. A *colloidal solution of tungstic acid* is obtained by treating sodium tungstate with hydrochloric acid, and dialyzing the mixture. The tungstic acid remains behind in the form of a colloidal solution, which, on evaporation,

forms a gummy mass. Tungsten also forms *polytungstic acids*, by the polymerization of tungstic acid and the loss of one or more molecules of water. Salts of the acid $H_2W_4O_{13}$ are known. This is obtained from four molecules of tungstic acid by loss of three molecules of water: —

$$4\,H_2WO_4 = 3\,H_2O + H_2W_4O_{13}.$$

Tungsten trioxide combines with other acids like molybdenum oxide, forming complex acids. The best known of these are the compounds with arsenic, phosphoric, and iodic acids. These are known as *phosphotungstates*, *arsenitungstates*, *iodotungstates*, etc.

URANIUM (At. Wt. = 238.5)

Uranium is characterized by the unusual variety of its compounds, and by the great number of spectrum lines which it produces. It has the highest atomic weight of any known element, and manifests the highest valency, being octivalent. This degree of valency is reached by only one or two other elements. It also manifests a great variety of valencies, ranging all the way from three to eight.

Uranium occurs in nature chiefly as the mineral *uranite* or *pitchblende*. This consists chiefly of the oxide U_3O_8.

The metal can be prepared by heating this oxide with carbon in an electric furnace; also by reducing the chloride with sodium or aluminium.

The metal has the color of silver, and the specific gravity 18.7. Finely divided uranium combines with oxygen at about 200°, burning readily in the gas.

Oxides of Uranium. — Uranium forms a number of compounds with oxygen and hydrogen. These frequently show basic properties towards strong acids, as well as acid properties towards strong bases.

Uranous oxide, UO_2, forms salts with acids in which the uranium is quadrivalent. Thus, we have uranous sulphate, $U(SO_4)_2$, oxalate, $U(C_2O_4)_2$, etc. When these salts are treated with an alkali the compound $U(OH)_4$ is precipitated.

When uranous oxide is heated it passes over into the compound U_3O_8.

When the compound U_3O_8 is treated with nitric acid, uranyl nitrate, $UO_2(NO_3)_2$, is formed. When uranyl nitrate is heated, the trioxide UO_3 is formed.

The compound $UO_2(OH)_2 = H_2UO_4$ acts as a base towards strong

acids — the group UO_2, known as the *uranyl group*, playing the part of a bivalent metal. Thus, we have uranyl sulphate, UO_2SO_4, uranyl nitrate, $UO_2(NO_3)_2$, etc.

The higher oxidation products of uranium also have acid properties towards strong bases. The compound H_2UO_4, or its derivatives, dissolve readily in strong bases, forming *uranates*.

The uranates are prepared by adding a base to a solution of a uranyl compound. These, however, are not derived from normal *uranic acid*, H_2UO_4, but from *pyrouranic acid*, $H_2U_2O_7$, which is obviously obtained from two molecules of the normal acid by loss of one molecule of water. The sodium salt $Na_2U_2O_7$ is used as a pigment for coloring glass under the name of *uranium yellow*.

Chlorides of Uranium. — Uranium forms three chlorides: the trichloride, UCl_3, the tetrachloride, UCl_4, and the pentachloride, UCl_5. The trichloride is obtained by reducing the tetrachloride with hydrogen. The tetrachloride is obtained from the pentachloride, which is formed by heating a mixture of uranium oxide and charcoal in a current of chlorine.

Uranium Radiation. — Compounds of uranium when exposed to light have the property of emitting an invisible radiation, which traverses many substances impervious to light, such as black paper, thin sheets of many metals such as aluminium, copper, etc. This property is possessed by metallic uranium to from three to four times the extent that it is manifested by the salts of this metal.

This is entirely different from the phosphorescence shown by salts of uranium, since the latter disappears very quickly, while the power of emitting this invisible radiation persists for years.

If a piece of uranium or of one of its salts is placed above a photographic plate covered with black paper or aluminium leaf, and various substances are interposed between the uranium and the plate, after several hours "radiographs" are obtained upon the plate. These rays were also supposed for a time to be capable of polarization by means of tourmalines. These phenomena would suggest properties analogous to those possessed by light, and led Stokes to conclude that the Becquerel rays occupy a position intermediate between the Röntgen rays and light. He regarded the Röntgen ray as made up of a great number in independent pulses. In the Becquerel ray he thought that there was still irregularity, but some regularity was beginning to manifest itself.

Later experiments, however, have shown that the uranium radiation undergoes neither reflection, refraction, nor polarization.

This radiation is transmitted differently through screens of dif-

ferent substances, depending upon the angle in which they are simultaneously placed in the path of the radiation. This would indicate that the radiation is not homogeneous.

The uranium radiation discharges positive and negative charges with equal speed, and its power to render a gas a conductor has been shown by Rutherford to be due to an ionization of the gas. The above and similar phenomena have been characterized as *radioactivity.*

Other Radioactive Substances. — The discovery was made in 1898 by G. C. Schmidt that thorium, like uranium and its compounds, can send out rays which are similar to the Rontgen rays. A little later (1898) M. and Mme. Curie observed that certain uranium minerals, such as pitchblende, were radioactive to a much greater degree than metallic uranium or thorium. The conclusion was drawn that in such minerals there are other radioactive substances than uranium, and an attempt was made to isolate such substances. Pitchblende was dissolved in acid, and hydrogen sulphide passed into the solution. The sulphide of the active substance is insoluble in ammonium sulphide, and was partially separated from the other sulphides insoluble in this substance. Further, when the mixed sulphides from pitchblende are heated to 700°, the active substance sublimes into the cooler portion of the tube. The substance obtained in this way was 400 times as active as uranium. This was further purified by removing the bismuth until a much greater radioactivity was shown. This substance was called *polonium,* after the native country of Mme. Curie.

M. and Mme. Curie discovered a second radioactive substance in pitchblende. This substance is obtained with the barium, from which it is impossible to effect a complete separation. This substance is not precipitated by hydrogen sulphide nor ammonium sulphide. By dissolving the chloride in water and precipitating with alcohol, a substance was obtained which had a radioactivity 17,000 times that of uranium. This substance they termed *radium.* The spectrum was determined by Demarcay, and new lines were discovered.

More recently Dabierne claims to have discovered a third radioactive substance in pitchblende, which is closely allied to titanium in its properties.

The rays from radium are much more intense than those from polonium, uranium, or thorium. Rays from radium and polonium produce fluorescence in barium platinocyanide, while those from thorium and uranium are not sufficiently intense to excite this

fluorescence. The radiation from polonium is much less penetrative than that from radium.

Some of the rays from certain radioactive substances are deviated by a magnetic field. Of these, a part are deviated the one way and a part the other, showing that some are charged positively and some negatively. The former are known as α rays, the latter as β rays. Certain rays from radium are not deviated by the magnetic field. These are much more penetrative than the deviable rays, and are known as γ rays.

Certain Remarkable Properties of Radium. — The most recent determination of the atomic weight of radium by physical means gives the value 257.8. This shows that the radium atom has the largest mass of any known atom. This would be expected, since the other well-known radioactive substances — uranium, thorium, and lead — have large atomic weights. Radium, being the most radioactive, would be expected to have the highest atomic weight.

A very remarkable property of radium is that it maintains itself at a *temperature higher than that of the surrounding medium.* This constant development of heat energy has been shown by Rutherford to come largely from the *emanation*, which can be driven out of the salts of radium by heat, and can be condensed in glass tubes surrounded by liquid air. The amount of heat evolved by radium, in a given time, has been measured by Curie and Dewar by allowing it to boil liquid hydrogen, and measuring the amount of gas set free. They have shown that radium sets free enough heat to melt its own weight of ice every hour.

The most remarkable property of radium, however, is that discovered by Ramsay and Soddy. *Helium is constantly being produced from radium salts.* This has since been confirmed by Curie and Deslandres, and is now established beyond question.

This is the first authentic case on record of the transformation of one elementary substance into another.

CHAPTER XXXVIII

COPPER, SILVER, GOLD

COPPER (At. Wt. = 63.6)

There still remain three elements in the first group of the Periodic System which have not thus far been studied. It is a defect in this system that these elements fall in the first group, since they are not closely allied to the remaining members from the chemical standpoint. There are, to be sure, certain analogies between copper, silver and gold, and the alkalies, but there are analogies between almost any two chemical elements. Were it not for the Periodic System we should never think of dealing with the above three elements in the same connection with sodium and potassium. When the Periodic System leads us to connect elements as unlike as copper and sodium, it is distinctly harmful, and detracts from, rather than adds to, our scientific knowledge of these elements.

Occurrence and Preparation of Copper. — Copper occurs in considerable quantity in the free condition. This is true on Lake Superior, in Siberia, Japan, and elsewhere. Copper occurs in large quantities as cuprous oxide, CuO, or *cuprite*, cupric oxide, *azurite*, and *malachite* the blue and green basic carbonates, as *chalcocite*, Cu_2S, and *chalcopyrite*, $CuFeS_2$. This is also known as *copper pyrites*.

Copper is prepared from the oxides very simply by heating with charcoal. From the sulphide it is much more difficult to obtain pure copper. The sulphide of copper usually contains iron sulphide and other impurities, and this still further complicates the problem. The sulphides are roasted until the iron and a part of the copper are converted into the oxide. When the roasted ore is heated with sand and charcoal the iron oxide is partly reduced, forms ferrous silicate with the sand, and disappears in the slag. The copper is for the most part in the form of the sulphide, but there is still some iron sulphide present. This is known as *matte*.

The matte is again roasted, converting more of the iron sulphide into oxide. It is again fused with sand, and this process repeated until the iron is removed.

The copper, which is now in the form of the sulphide, is partially converted into the oxide, when the following reaction between the sulphide and oxide takes place: —

$$Cu_2S + 2\,CuO = SO_2 + 4\,Cu.$$

The copper thus prepared may be again heated with sand and charcoal, again reduced, and so on until a fairly pure copper is obtained.

Copper is finally purified by means of electrolysis. The impure copper obtained by the process just described is moulded into the form of large, thick plates, known as the "anode plates." These are suspended in a large bath of copper sulphate and connected with the positive pole of a dynamo. Between these plates are alternately suspended thin sheets of pure copper, which are the cathodes, and these are connected with the negative pole of the dynamo. When the current is passed copper is deposited upon each of the cathodes, and dissolves from each of the anodes. The action of the current is really to carry the copper from the anode to the cathode opposite to it, and deposit it upon the cathode.

Under these conditions the impurities are not deposited with the copper, but either remain in solution or are deposited in the form of a viscous mass on the bottom of the copper sulphate bath. These anode "slimes," as this material is termed, are worked over for various substances, and especially for gold and silver, which are often present in considerable quantity.

Properties of Copper. — Copper differs in color from all other metals, being a peculiar shade of red known as copper-red. Copper is quite resistant to chemical reagents. In contact with moist air it becomes covered with a green basic carbonate. When heated in the air it forms the oxide. Copper is readily acted on by nitric acid, but is not readily attacked by hydrochloric or sulphuric acid unless it is hot. Copper is easily attacked by sulphur compounds, forming the sulphide.

Copper does not decompose water until a white heat is reached, and then only slowly. Consumed in appreciable quantities, copper ions are poisonous.

On account of its physical properties, copper is one of the most valuable of the metals. It can be readily hammered into thin sheets or drawn into wire, and is very strong. Copper is not very heavy, having a specific gravity of 8.9. It melts at 1057°, and can, therefore, be easily cast. Next to silver copper is the best conductor of electricity, and is extensively used in this capacity in connection with telegraphy and telephony, and especially in connection

with electric lighting and electrotraction, where large amounts of electrical energy must be transported. This is one of the most important uses of the element copper.

Alloys of Copper. — Copper forms a number of alloys with the metals, which are very valuable. One of the best known is *brass*, which is an alloy of copper and zinc, containing generally about twice as much copper as zinc; but this varies greatly from one specimen to another. *German silver* or *argentan*, as we have seen, is an alloy of copper, nickel, and zinc, while *China silver* is argentan containing some silver. Copper also forms alloys with nickel and silver. These are frequently used for *coins*. The silver coins usually contain about ten per cent of copper.

Among the best-known alloys of copper are the *bronzes*. The ordinary bronzes are alloys of copper and tin, containing from ten to thirty per cent of tin. Bronzes used for statues also contain zinc. Among the alloys of copper and tin are *bell metal*, *spiegel bronze*, etc. *Manganese bronze* is an alloy of copper and zinc, to which manganese is added. *Phosphorus bronzes* are ordinary bronzes containing phosphorus.

Aluminium bronze is an alloy of copper, containing from six to eight per cent of aluminium. It is of a yellow color, resembling gold in appearance.

An alloy of copper and tin, containing about ten per cent of tin and ninety of copper, is known as *gun-metal*.

Oxides of Copper. — Copper forms two compounds with oxygen; cuprous oxide, Cu_2O, and cupric oxide, CuO. These are types of the two classes of copper compounds — the *cuprous compounds* in which copper is univalent, and the *cupric compounds* in which the copper is bivalent. Copper, therefore, forms two kinds of ions; the cuprous ion, $\overset{+}{Cu}$, and the cupric ion, $\overset{++}{Cu}$. Of these the cupric condition, in which the copper carries two electrical charges, is the more stable.

Cuprous oxide can be readily obtained by reducing an alkaline solution of a cupric salt with a mild reducing agent, such as cane-sugar. Cuprous oxide is a yellowish-red powder. When treated with an acid, like sulphuric acid, it forms cupric ions and metallic copper: —

$$Cu_2O + H_2SO_4 = H_2O + Cu + \overset{++}{Cu},\ \overset{=}{SO_4}.$$

Cupric oxide is formed by oxidizing copper in the air or in a stream of oxygen. Also by decomposing a cupric salt by heat. It is a black powder, which readily gives up its oxygen to reducing agents.

When cupric oxide is heated in a current of hydrogen it is readily reduced to metallic copper, the hydrogen being oxidized to water.

Cupric Hydroxide, $Cu(OH)_2$, is formed by treating a cupric salt with an alkaline hydroxide: —

$$CuCl_2 + 2\,KOH = 2\,KCl + Cu(OH)_2.$$

Cupric hydroxide is light blue in color, easily passing over into cupric oxide. When the liquid around the cupric hydroxide is heated this transformation takes place — the blue hydroxide becoming black in color, due to the formation of the oxide: —

$$Cu(OH)_2 = H_2O + CuO.$$

Cupric hydroxide is a very weak base, forming salts with acids which are strongly hydrolyzed. The hydroxide does not form normal salts with weak acids, but basic salts. Although cupric hydroxide is a weak base towards acids, it is not an acid towards bases, as is generally the case. It does not dissolve in alkalies.

Chlorides of Copper. — Both the cuprous and cupric ions combine with chlorine, and we have cuprous chloride, $CuCl$, and cupric chloride, $CuCl_2$.

Cuprous chloride is formed by reducing a cupric salt. When copper sulphate is mixed with sodium chloride and sulphur dioxide conducted into the mixture, cuprous chloride is formed. This appears as a white, crystalline compound when the above solution is poured into water. Cuprous chloride is also formed when hydrochloric acid is treated with an excess of copper, and the resulting solution poured into water.

It readily combines with oxygen, passing into the cupric condition, which is shown by the appearance of the blue color that is characteristic of the cupric ion, $\overset{++}{Cu}$. Cuprous chloride boils at about 1000°, and a determination of the density of its vapor gives a molecular weight corresponding to the double formula Cu_2Cl_2.

Cuprous chloride not only absorbs oxygen, but also carbon monoxide, forming the compound $Cu_2Cl_2 . CO . 2\,H_2O$.

Cupric Chloride, $CuCl_2 . 2\,H_2O$, is formed when cuprous chloride is treated with chlorine, or when cupric hydroxide is dissolved in hydrochloric acid: —

$$Cu(OH)_2 + 2\,HCl = CuCl_2 + 2\,H_2O.$$

Cupric chloride crystallizes in blue needles containing two molecules of water. When the water is driven off the anhydrous salt is yellow or yellowish-brown.

The solution of cupric chloride presents certain interesting color phenomena. Dilute solutions are blue, like the dilute solutions of all cupric salts. This is the color of the cupric ion. More concentrated solutions are green. This is due to the mixture of blue cupric ions and yellow, undissociated molecules of cupric chloride. If concentrated hydrochloric acid is added to the green solution of cupric chloride its color changes to yellowish-brown. By thus adding an excess of chlorine ions the dissociation of the cupric chloride is greatly driven back, according to the law of mass action, and the color of the undissociated molecules of the salt makes its appearance. Heat has the same influence as an excess of chlorine ions, driving back the dissociation. When a blue solution of cupric chloride is heated it therefore becomes green, and a green solution more and more yellow. These color phenomena are of interest in connection with the theory of electrolytic dissociation.

Cupric chloride combines with ammonia, forming complex compounds, such as $CuCl_2 . 2\,NH_3$, $CuCl_2 . 6\,NH_3$, etc.

Sulphides of Copper. — Cuprous sulphide, Cu_2S, occurs in nature. It is known as *copper-glance*. It is formed by reducing cupric sulphide in a current of hydrogen.

Cupric sulphide, CuS, is formed when hydrogen sulphide is passed into a solution of a copper salt: —

$$CuCl_2 + H_2S = 2\,HCl + CuS.$$

Copper sulphide is a black, amorphous powder, which is insoluble in dilute acids. It is therefore precipitated from a solution of a neutral copper salt by hydrogen sulphide. It readily takes up oxygen, forming copper sulphate.

Copper Sulphate, $CuSO_4 . 5\,H_2O$. — This is the best known of all the compounds of copper, and one of the best-known substances. Copper sulphate or *blue vitriol*, as it is called, is formed when sulphuric acid acts on metallic copper. The hydrogen is not set free but acts on more sulphuric acid, reducing it to sulphur dioxide: —

$$Cu + H_2SO_4 = CuSO_4 + H_2,$$
$$H_2SO_4 + H_2 = 2\,H_2O + SO_2.$$

Copper sulphate crystallizes from the solution in the form of beautiful blue crystals containing five molecules of water — $CuSO_4 . 5\,H_2O$. When the sulphate is heated it loses four molecules of water at 100°, but the fifth is retained until 200° is reached. When the last molecule of water is driven off the salt also loses some sulphuric acid.

When in contact with a sulphate which crystallizes with seven molecules of water, the salt, $CuSO_4 . 7\,H_2O$ separates. Copper sulphate in solution is blue, and this is due to the color of the cupric ions. The salt with water of crystallization is blue, probably due to a slight *dissociation of the salt in its water of crystallization.* Anhydrous copper sulphate is white, and this is the color of the molecules of the salt. When the white, anhydrous salt is dissolved in water it is dissociated to a greater or less extent, and the blue color of the copper ion appears.

Copper sulphate combines with ammonia, forming the compounds $CuSO_4 . 4\,NH_3$, and $CuSO_4 . 2\,NH_3$. Copper sulphate in solution is a good conductor of the electric current, and from such a solution the copper is easily deposited *electrolytically.* This is a convenient method of determining copper. We have seen that copper sulphate is used as the electrolyte in purifying copper by the electrolytic method.

Copper Carbonate. — A soluble carbonate added to a solution of a copper salt does not precipitate normal copper carbonate, but a basic carbonate — $Cu_2(OH)_2(CO_3)$. This is the composition of the mineral *malachite,* which has a beautiful green color and is used for ornamental objects. It occurs in large quantities, especially in Siberia. Another less basic carbonate is known as *azurite,* having a beautifully blue color. It has the composition $Cu_3(OH)_2(CO_3)_2$. Azurite is also useful in making ornamental objects.

Other Copper Salts. — The *acetate of copper* has the composition $Cu(CH_3COO)_2$, and is known as *verdigris.* The term verdigris has also been applied to the basic acetate of copper. It is prepared by the action of acetic acid on copper in the presence of the air. *Copper acetylene,* Cu_2C_2, is the cuprous salt of acetylene, in which the hydrogen ions are replaced by cuprous copper. It is prepared by passing acetylene into ammoniacal cuprous oxide. It is an explosive compound.

Copper ferrocyanide, $Cu_2Fe(CN)_6$, has already been referred to in connection with the preparation of semi-permeable membranes for measuring osmotic pressure. It is formed by adding a soluble cupric salt to a solution of potassium ferrocyanide: —

$$2\,CuSO_4 + K_4Fe(CN)_6 = 2\,K_2SO_4 + Cu_2Fe(CN)_6.$$

It is a reddish-brown, gelatinous mass, which, in color and general appearance, resembles ferric hydroxide. As we have seen, it is the best substance known with which to prepare semi-permeable membranes for demonstrating and measuring osmotic pressure.

Precipitation of Copper by Zinc. — When a bar of zinc is immersed in a solution of a copper salt, copper is precipitated upon the zinc, and the zinc dissolves. This is due to the high solution-tension of the zinc, and the low solution-tension of the copper. Zinc, having a high solution-tension, sends ions into the solution, while copper with its very low solution-tension is forced out of the solution. There is a general principle involved here. *A metal precipitates from their salts those metals which stand below it in the tension-series, and is precipitated by those metals which stand above it in the same series.* If the metals stand too close together in this series, they cannot precipitate the lower member from its salts. There must be a considerable difference in position in the series in order to have precipitation. This principle is important to bear in mind, since it enables us to say at once just what will happen when any metal is immersed in a salt of any other metal. The simplest method of recalling the principle is to remember that those metals with great solution-tension, precipitate from their salts the metals with small solution-tension.

Another Method of Ion Formation. — The precipitation of one metal from its salts by another metal furnishes us with a means of forming ions. When zinc replaces copper from its salts the zinc atom takes the charge from the copper ion, becoming itself an ion, while the copper is converted into an atom: —

$$Zn + \overset{++}{Cu}, \overset{=}{SO_4} = Cu + \overset{++}{Zn}, \overset{=}{SO_4}.$$

This is the third method of ion formation with which we have had to deal (111 and 425). It can be formulated thus: *An atom takes the electrical charge from an existing ion, becoming itself an ion, while the former ion is converted into an atom.*

There still remains one other method by which ions can be formed. This will be taken up under gold.

CHAPTER XXXIX

SILVER AND GOLD

SILVER (At. Wt. = 107.93)

We now come to the so-called "noble metals" or "precious metals." The well-known elements silver and gold will now be studied.

Silver is not among the rare elements. It occurs in nature in considerable abundance and in a number of compounds. The most important of these is the sulphide, Ag_2S, *argentite*, the double sulphide of silver and antimony, Ag_3SbS_3, *pyrargyrite*, the double sulphide with copper, CuAgS, *stromeyerite*, and the chloride of silver, AgCl, *horn-silver*. Silver also occurs in nature in the free condition in certain localities in the United States, Norway, etc.

Preparation of Silver. — A large number of methods have been devised and used for obtaining pure silver. The method employed depends upon the nature of the silver ore which is being used.

If the chloride is employed, the silver is precipitated by means of iron or lead.

If the sulphide is used, this is either roasted in the air and converted into the sulphate, and the silver precipitated by metallic iron, or it is converted into the chloride and the silver precipitated by iron.

When silver is set free along with many other substances, it is frequently dissolved in mercury and the mercury then distilled off. This is known as the *amalgamation process*.

Lead ores, especially galena, usually contain silver, and silver is frequently obtained mixed with lead. The solution of silver in lead is concentrated by allowing it to crystallize. Pure lead separates at first, and the remaining solution becomes richer and richer in silver. A concentration of the silver in the lead is finally attained, where the crystals which separate have the same concentration of silver as the remaining solution.

When this stage is reached it is impossible to effect further separation by crystallization. The above process of fractional crystalli-

zation, known as the *Pattinson process*, can be continued until the solution contains about one per cent of silver.

To effect further separation the lead solution of silver is heated on the air. The lead is oxidized to litharge, and allowed to flow away or be absorbed by the porous walls of the cupel in which the oxidation takes place. This process is known as *cupellation*.

Another method of separating silver from lead is to fuse the latter with zinc (Parke's method). Silver dissolves readily in zinc, forming a solid solution, and the zinc solution of the silver floats on the lead and can be removed mechanically. The zinc can be dissolved out by means of dilute acids, or oxidized hot by means of steam, leaving the silver behind.

Silver is prepared in pure condition by one of two processes: either by dissolving it in concentrated sulphuric acid and precipitating the metal by iron, or by the *electrolytic process*. This consists in casting the impure silver in anodes and using pure sheet silver as the cathodes. The electrolyte is a nitric acid solution of silver nitrate, to which copper nitrate is added to increase its conductivity. The silver separates upon the cathode in the form of beautiful crystals.

Properties of Silver. — Silver is a white metal with a high lustre. It has the specific gravity 10.57 when distilled, and melts at about 1000°. It is not as hard as copper, and of all the metals is the best conductor of heat and electricity. It can be easily drawn into wire or hammered into thin foil. When melted in the presence of the air silver absorbs large volumes of oxygen; indeed, as much as fifteen or twenty times its own volume. When the metal cools the oxygen is given out, and this is known as the *spitting of silver*.

Silver is not easily attacked by chemical reagents. It is not attacked by the strongest alkalies even when hot, nor by dilute acids, with the exception of nitric acid. Concentrated nitric acid easily converts it into the nitrate, and concentrated sulphuric acid into the sulphate, the acid being reduced to sulphur dioxide as with copper: —

$$2\,Ag + 2\,H_2SO_4 = 2\,H_2O + SO_2 + Ag_2SO_4.$$

Silver combines directly with sulphur, forming silver sulphide. This can be seen by holding a moist silver coin in a current of hydrogen sulphide. It also combines directly with the halogens at ordinary temperatures. Silver dissolves readily in a solution of potassium cyanide.

Colloidal Silver. — A number of solutions of silver in water have been described, which have all of the properties of colloidal solutions

These have been prepared by Lea and others by reducing silver salts. The citrate heated in a current of hydrogen, or reduced by ferrous sulphate, yields a colloidal solution of silver in water. Lea prepared solutions of silver which have very different colors and somewhat different properties. From these solutions ordinary silver is easily obtained. Another method of preparing colloidal solutions of silver has recently been devised by Bredig. Two bars of silver are immersed in water and their lower ends placed close together. An electric current is passed between the bars, when metallic silver is torn off in such a fine state of division in the water, that a drop of the solution appears homogeneous under the microscope.

From such a colloidal solution of silver the metal is obtained by boiling with hydrochloric acid. Such solutions have remarkable catalytic action, as we shall see when we come to study platinum.

Alloys of Silver. — Silver forms a number of valuable alloys. The alloy with mercury or the amalgam occurs in nature, and can also be readily prepared by bringing the two metals into contact. The alloy with copper, which is used in making coins, has already been referred to. The alloy with aluminium can be used for soldering aluminium.

Silvering. — Silver, as we have seen, is quite resistant to ordinary chemical agents. It is, consequently, used for making utensils and objects of ornament. These are, however, expensive, and *silver-plated* wares are much used in their stead. These consist of brass, copper, or other metallic objects covered completely with metallic silver. They, therefore, have the properties of silver objects.

Silver-plating finds extensive application. The silver is deposited by a number of methods; the silver is reduced directly upon the object to be plated, or it is applied mechanically and pressed upon the object while hot. Another method is to apply the silver in the form of an amalgam and then distil off the mercury; while still another method which is extensively used is the electrolytic. Silver is deposited electrolytically from a solution of the cyanide dissolved in potassium cyanide.

Silver is now being extensively deposited upon glass in the construction of *mirrors*. The glass surface must be entirely freed from grease and all other impurities, and is then treated with ammoniacal silver nitrate to which some caustic soda and a mild reducing agent have been added. The reducing agents generally employed are aldehyde ammonia, or sugar of milk. The silver is slowly thrown out of its salt and deposited uniformly upon the glass surface in the form of a coherent layer with a bright surface. The *silvering of glass* is

important in connection with optical apparatus, since such surfaces are good reflectors of light. It is also finding increasing application in connection with the preparation of ordinary mirrors, taking the place of mercury, which is very poisonous.

Oxides and Hydroxide of Silver. — Silver forms three compounds with oxygen: the suboxide, Ag_4O, the normal oxide, Ag_2O, and the superoxide, AgO. It, however, forms only one hydroxide — AgOH, which is stable only at very low temperatures. The hydroxide is thrown down when an alcoholic solution of caustic potash is added to an alcoholic solution of silver nitrate at a low temperature (— 40°). At all ordinary temperatures silver hydroxide loses water, forming black silver oxide: —

$$2\,AgOH = H_2O + Ag_2O.$$

Silver hydroxide is a strong base, its salts not being hydrolyzed by water. In this respect it resembles the alkalies. Silver oxide is sufficiently soluble to give a strongly alkaline reaction. Such a solution must contain silver and hydroxyl ions.

The silver ion is univalent, combining with the anions of acids and forming salts of the general type: AgCl, $AgNO_3$, Ag_2SO_4, etc. It is of interest to note that when atoms of silver pass over into ions of silver a large amount of heat is absorbed — the reaction is endothermic. The silver ion is especially a reagent for the halogen ions. It combines with them, forming stable, insoluble compounds, which we shall now study.

Silver Chloride, AgCl, is formed whenever a silver ion comes in contact with a chlorine ion: —

$$\overset{+}{Ag} + \overset{-}{Cl} = AgCl.$$

It is a white precipitate which quickly darkens when exposed to the light. The darkening is due to the formation of a subchloride of silver, Ag_2Cl, or Ag_4Cl.

Silver chloride is practically insoluble in water, and is consequently used to determine quantitatively both silver and chlorine. It is readily soluble in aqueous ammonia, and is thus distinguished from the bromide and iodide.

Silver Bromide, AgBr. — Silver bromide is precipitated when silver ions come in contact with bromine ions: —

$$\overset{+}{Ag} + \overset{-}{Br} = AgBr.$$

Silver bromide is white, with a slightly yellowish tint; is soluble with difficulty in ammonia and almost insoluble in water. Silver

bromide is even more sensitive to light than silver chloride, and upon this fact is based its use in photography.

Photography. — The science of photography is based almost exclusively upon the action of light on silver bromide. The "sensitive film" is prepared by adding ammonium bromide to gelatine, and then adding silver nitrate in the dark. The following reaction takes place: —

$$NH_4Br + AgNO_3 = NH_4NO_3 + AgBr.$$

The silver bromide is distributed through the gelatine in a very fine state of division. The mass is then warmed until the precipitate has become sufficiently coarse-grained — the coarser the grains the more sensitive to the action of light. The soluble salts, ammonium nitrate and silver nitrate, are removed by washing with water, and the fused mass is then poured upon the surface of glass plates, to which it adheres in the form of a thin film.

The plate containing the film is then exposed to the action of the light from the object which it is desired to photograph. The time of the exposure depends upon the intensity of the light and the sensitiveness of the film. It may vary from several seconds to a hundredth of a second, or even less. The action of the light is probably to reduce the silver bromide to a sub-bromide of silver, although this is not proved.

The exposed plate is now treated with a "developer," which consists of some reducing agent, such as pyrogallic acid, ferrous sulphate, etc. The object of the developer is to reduce the silver bromide depositing metallic silver, and the whole science of photography depends upon the fact that the silver bromide which is most strongly illuminated, is most readily reduced by the developer. Where the object was brightest, the plate is covered with a deeper film of metallic silver, which becomes less and less dense as the illumination is less and less. The result is a photograph of the object with the light parts dark and the dark parts light. This is the so-called "negative." The negative thus obtained still contains unreduced silver bromide, since the portion of the salt which was not exposed to the light is not reduced by the developer. If the negative is exposed to the light in this condition, the silver bromide would be acted upon, and the original picture would be destroyed by superimposed images. To avoid this the negative must be *fixed*. *i.e.* treated with a solution of a substance which will dissolve the unreduced silver bromide. The fixing agent usually employed is a solution of sodium thiosulphate, $Na_2S_2O_3$, known technically as "hyposulphite," or even as "hypo." This acts upon the silver

bromide, forming the double salt, $Ag_2S_2O_3 . 2 Na_2S_2O_3$, which is quite soluble in water and is easily removed when the plate is washed with running water. The negative is now "fixed," and ready to be used in making "prints" or "positives." A "positive picture," or a photograph proper, is obtained by placing the negative above paper covered with the sensitive film and exposing it to light. The dark parts of the negative cut off the light and appear bright on the positive picture, and, conversely, the light parts appear dark, since much light passes through and acts upon the sensitive film upon the paper. The positive, therefore, represents the lights and shades in the order in which they occur in the object, and is a true picture in metallic silver of that object.

In some cases the print is immersed in a bath containing a gold or platinum salt, when the silver precipitates the gold or platinum, itself passing into solution. Such photographs have, then, the soft brown color of finely divided gold, or the harder, steel-gray tint of finely divided platinum.

Photography not only finds extensive application in the arts, but is of fundamental importance in scientific investigations. Many epoch-making discoveries in physics, chemistry, astronomy, and biology could have never been made without the use of the camera. As an example, the whole science of spectrum analysis, as we know it to-day, depends for its existence largely upon photography.

Silver Iodide, AgI, is formed whenever silver and iodine ions come in contact. It is a yellow solid, insoluble in water and in ammonia. Silver iodide, like the bromide and chloride, is sensitive to light, and was formerly used in connection with photography. Indeed, the earliest method of preparing photographs, devised by *Daguerre*, made use of silver iodide. A plate of silver was exposed to the vapors of iodine, when it became covered with a layer of silver iodide. It was then exposed to the light reflected from the object to be photographed. The silver iodide was reduced, and strongest where the illumination was greatest. The plate was then exposed to the vapors of mercury. The mercury combined with the silver, and appeared bright where the reduction was the greatest. By this means a *daguerreotype* was produced, which was bright where the illumination was greatest and dark where it was least.

Silver iodide has been practically abandoned in the preparation of sensitive films, silver bromide being used almost exclusively.

Silver Nitrate, $AgNO_3$, is formed when silver is dissolved in concentrated nitric acid. It crystallizes in beautiful, colorless plates, melting at 200°. It is, therefore, frequently moulded into thin

cylinders, and thus comes on the market under the name of *lunar caustic.* When brought in contact with organic matter silver nitrate is readily reduced, metallic silver being deposited. It also forms insoluble compounds with albuminoids. We can now understand why the hands are blackened by contact with silver nitrate, and why it is used to cauterize small wounds and stop the flow of blood.

Silver Sulphide, Ag_2S, is precipitated as a black powder by the action of hydrogen sulphide on a solution of a silver salt. It is insoluble in water and in dilute acids, and, therefore, silver belongs in the class of elements whose sulphides are precipitated from neutral salts by hydrogen sulphide. Moist silver combines directly with sulphur and forms the sulphide, and hydrogen sulphide acts upon a moist silver coin, producing the black sulphide. Silver is, therefore, frequently used to detect the presence of sulphur.

Silver Sulphate, Ag_2SO_4, is formed by dissolving silver in hot, concentrated, sulphuric acid. It is only slightly soluble in water.

Silver Carbonate, Ag_2CO_3, is formed whenever silver ions are brought in contact with carbonic ions, $\overset{=}{CO_3}$: —

$$2\,AgNO_3 + Na_2CO_3 = 2\,NaNO_3 + Ag_2CO_3.$$

It is a yellow solid insoluble in water.

Other Compounds of Silver. — The silver salt of triazoic acid, *silver triazoate,* AgN_3, is formed by adding the acid to a soluble silver salt: —

$$AgNO_3 + HN_3 = HNO_3 + AgN_3.$$

The salt resembles silver chloride in appearance, but is unstable and very explosive.

Silver cyanide, AgCN, is formed as a white solid by the action of silver ions on cyanogen anions: —

$$\overset{+}{Ag},\ \overset{-}{NO_3} + \overset{+}{K},\ \overset{-}{CN} = \overset{+}{K},\ \overset{-}{NO_3} + AgCN.$$

Silver cyanide readily dissolves in an excess of potassium cyanide, forming a *double cyanide,* which is soluble. This has the composition $KAg(CN)_2$. This double salt is used for electroplating objects with silver. In solution it breaks down into potassium and silver cations, and cyanogen anions, and the silver is deposited as a uniform, coherent layer on the object which it is desired to cover with silver.

Silver Sulphocyanate, AgSCN, is precipitated as a white solid when silver and sulphocyanogen ($\overset{-}{SCN}$) ions come in contact: —

$$\overset{+}{Ag},\ \overset{-}{NO_3} + \overset{+}{NH_4},\ \overset{-}{SCN} = \overset{+}{NH_4},\ \overset{-}{NO_3} + AgSCN.$$

Silver sulphocyanate is made use of in determining silver quantitatively. A standard solution of ammonium sulphocyanate is added, drop by drop, to a solution of the silver salt containing some ferric ions[1] (ammonium iron alum) and nitric acid. As soon as all the silver is precipitated the sulphocyanogen ion reacts with the ferric ion, forming iron sulphocyanate, which is characterized by its blood-red color. The appearance of this color shows that all of the silver has been precipitated. Knowing the volume of the solutions of ammonium sulphocyanate used, and its strength, we have all the data necessary for calculating the amount of silver present. Such a quantitative method is known as a *volumetric method,* and from its discoverer as *Volhard's method.*

Silver chromate, Ag_2CrO_4, is also useful in quantitative analysis on account of its red color. When a solution of silver nitrate is added to a solution of a chloride containing chromate ions (potassium chromate), the color of the silver chromate will appear as soon as all of the chloride is precipitated. In this way either the amount of the silver ions or that of the chlorine ions can be determined by having a standard solution of the other ion. This is known from its discoverer as the *Mohr method* of determining silver.

GOLD (At. Wt. = 197.2)

The element gold is one of the "noble metals," and is frequently classed with platinum and allied elements. On the whole, however, it seems best to study gold in connection with copper and silver.

Gold occurs in nature chiefly in the uncombined condition, in the form of nuggets or grains in quartzite rocks or in sands. It also occurs combined with the element tellurium, as the *telluride.* When it occurs native it is by no means pure, containing silver, copper, etc.

The Metallurgy of Gold. — Gold occurs usually in very small quantities, and widely distributed through a large mass of rock or sand. It must be obtained free from large quantities of foreign substances. This is accomplished by *placer mining* and by *vein mining.* In placer mining the earth or sand is washed with water, the light materials being carried away and the gold left behind with the heavier substances. In *hydraulic mining* the gold-bearing earth and sands are washed down from the hills by water under pressure, and

[1] A very large excess of the ammonium iron alum is added to make the reaction more sensitive. This is an excellent example of the *effect of mass* as utilized in quantitative analysis.

the heavy gold collected by dissolving it in mercury. The gold is obtained from the amalgam by distilling off the mercury. When the gold occurs in veins in the quartz, this is finely powdered and then treated with mercury. Gold amalgam is formed, and the gold obtained by distilling off the mercury.

It not infrequently happens that the *amalgamation process* does not work satisfactorily on account of the nature of the impurities present with the gold. If arsenic is present the *chlorination process is used.* This consists in treating the gold ore with chlorine, bleaching-powder, and sulphuric acid; the gold chloride formed being dissolved in water. Gold is obtained from the chloride by reduction with ferrous sulphate or carbon, or by precipitation with hydrogen sulphide as the sulphide, and heating the sulphide.

If other impurities are present, especially tellurium, the *cyanide process* is used. This consists in treating the gold ore with potassium cyanide, in which finely divided gold readily dissolves. The gold is precipitated from the cyanide solution by means of metallic zinc, or electrolytically, and then subjected to cupellation. Gold thus obtained is impure and must be *purified.* The silver can be removed by dissolving it out in nitric acid or concentrated sulphuric acid. If the amount of gold in the alloy exceeds twenty-five per cent, this does not work satisfactorily. In such cases the alloy is fused with enough silver to dilute the gold to not more than one-fourth. The process is therefore called *quartation.*

Another method of separating silver from gold is to dissolve the alloy in aqua regia, and to treat the solution, after evaporating the nitric acid, with a reducing agent such as ferrous chloride: —

$$3\,FeCl_2 + AuCl_3 = 3\,FeCl_3 + Au.$$

Properties of Gold. — Gold is a soft, yellow solid, melting at 1064° and forming a greenish liquid. It has a very high specific gravity — 19.3. Gold is extremely malleable, and can be hammered into leaves not more than two-millionths of a millimetre in thickness. Such gold leaf is translucent and has a green color.

Gold is very resistant chemically, being attacked by comparatively few substances. Gold is not attacked by any of the strong mineral acids. It dissolves in chlorine water, aqua regia, caustic alkalies, nitrates, and cyanides.

The solution of gold in chlorine water is of special interest, since it represents a *fourth and the last mode of ion formation.* Gold has a very low solution-tension, and, therefore, sends very few ions into

solution. Chlorine water does not conduct the electric current, and, therefore, the chlorine is not ionized. When the molecules of gold come in contact with the molecules of chlorine, the former become cations and the latter anions: —

$$Au + Cl + Cl + Cl = \overset{+++}{Au}, \overset{-}{Cl}, \overset{-}{Cl}, \overset{-}{Cl}.$$

A molecule of a substance which can form cations comes in contact with a molecule of a substance which can form anions, and both are ionized.

A *colloidal solution* of gold is readily prepared by reducing a dilute alkaline solution of the chloride with formic aldehyde, and removing the crystalloids formed by dialysis. It is readily prepared by the method of Bredig, to be described under platinum. Two bars of gold are brought close together under water, and a considerable electric current passed between them through the water. The gold is torn off in a very fine state of division, and there results a colloidal solution of the metal. The properties of such solutions will be described more fully under platinum. A mixture of colloidal gold and colloidal stannic acid is known as the *purple of Cassius.*

Gold forms *alloys* with a number of the metals. The best known and most important are the alloys with copper and silver. Pure gold is too soft for use either as coin or as ornamental objects. To make it harder and more durable, copper is added. This gives to the gold a deep-red color. The alloy containing ten per cent of copper is frequently used. The purity of the gold is expressed in *carats*, pure gold being 24 carats. The number of carats means the number of parts of gold in 24 parts of the alloy. Thus, 18-carat gold means an alloy containing 18 parts gold and 6 parts copper.

The alloy of gold and silver is extensively used instead of pure gold, being more resistant to abrasion and more durable.

Gold Plating. — Metal objects are covered with gold in the same manner and for the same purpose that they are covered with silver. Gold plating has been effected by a number of methods, but these have practically all given place to the electrical. The object to be electroplated with gold is made the cathode, and a piece of pure gold the anode, the double cyanide of gold and potassium being the electrolyte.

The object of plating the ordinary metals, such as copper, brass, etc., is twofold. The gold-plated metal has the appearance of solid gold, with all of its attractive features. Further, such objects are resistant to chemical reagents, the covering of gold protecting the less resistant metal beneath.

Oxides and Hydroxides of Gold. — Gold forms the two oxides Au_2O and Au_2O_3, which are typical of the univalent and trivalent compounds of gold. It also forms the corresponding hydroxides, $Au(OH)$ and $Au(OH)_3$. Although these compounds are weak bases, combining with the anions of certain acids and forming salts, the auric hydroxide also has acid properties. Auric oxide and hydroxide dissolve in caustic alkalies, forming *aurates.* These are salts of the acid $HAuO_2$, which is $Au(OH)_3$ minus water: —

$$Au(OH)_3 = H_2O + HAuO_2,$$
$$HAuO_2 + NaOH = H_2O + NaAuO_2.$$

Salts of Gold. — Gold forms the aurous ion $\overset{+}{Au}$, and the auric ion $\overset{+++}{Au}$. One of these carries one electrical charge, or is univalent, and the other carries three electrical charges, or is trivalent. These ions can form salts with the anions of certain acids, and a few of these will be considered.

The aurous ion, $\overset{+}{Au}$, combines with chlorine and forms *aurous chloride,* $AuCl$. This compound is prepared by carefully heating auric chloride to 180°. This decomposes into aurous chloride and chlorine. Aurous chloride combines with the chlorides of the alkalies, forming double chlorides of the composition $MAuCl_2$.

Auric chloride, $AuCl_3$, is prepared by dissolving gold in aqua regia and gently heating the resulting product to remove hydrochloric acid. The compound formed by the action of aqua regia on gold has the composition $HAuCl_4$, and is known as *hydrochlorauric acid.* This compound can be easily isolated in the form of yellow crystals, and many salts of this substance are known. Thus, we have $KAuCl_4$, $NaAuCl_4$, etc. These have been regarded as double chlorides of gold and the alkalies, but are well-defined salts of a well-characterized acid, which can be readily obtained.

Gold forms two compounds with sulphur, aurous and auric sulphides. *Aurous sulphide,* Au_2S, is formed by the action of hydrogen sulphide on a hot solution of a salt of gold. It is light gray in color. When the solution of the gold salt is cold, the compound Au_2S_2 is precipitated as a black powder. Aurous sulphide dissolves in alkali sulphides, forming compounds of the type $MAuS$, which are soluble in water. The compound Au_2S_2 dissolves in yellow ammonium sulphide, forming the compound NH_4AuS_2, which is soluble in water. This is important in connection with the detection and separation of gold.

CHAPTER XL

LEAD, TIN

LEAD (At. Wt. = 206.9)

There remain two elements in group IV which have not been studied. These are tin and lead. Although the atomic weight of tin is less than that of lead, its chemistry is more complex, and it will be considered after lead.

Occurrence, Preparation, and Properties of Lead.—Lead occurs in nature in a number of compounds. The most important is the sulphide PbS, or *galena*. It also occurs as the carbonate $PbCO_3$, *cerussite;* the chromate $PbCrO_4$, *crocoisite;* the molybdate $PbMoO_4$, *wulfenite;* and in other forms.

Galena, being the principal ore of lead, is the one from which most of the lead of commerce is prepared. Several methods are employed to obtain the lead from the sulphide. One method is to roast the sulphide, converting it into the oxide, and then reduce the oxide with carbon:—

$$2\,PbS + 3\,O_2 = 2\,PbO + 2\,SO_2,$$
$$PbO + C = CO + Pb.$$

A second method is to roast the sulphide until a part of it is converted into the oxide, and then heat the oxide with the sulphide:—

$$PbS + 2\,PbO = 3\,Pb + SO_2.$$

In the above process a part of the lead is converted into the sulphate. This also yields metallic lead when heated with the sulphide:—

$$PbSO_4 + PbS = 2\,SO_2 + 2\,Pb.$$

The separation of silver from lead has been considered under silver.

Lead is a very soft, bluish-white metal, which melts at 335°. It has a fairly high specific gravity, 11.4. It becomes coated with a layer of oxide when exposed to the air at ordinary temperatures, and readily combines with oxygen when melted in the presence of the

air. The action of water upon lead is of hygienic importance. Pure water dissolves lead much more readily than ordinary, impure water, such as that in springs, rivers, etc. The impurities react with the lead and form a coating of carbonate, sulphate, etc., which protects the metal from the further action of the water. If the water contains free carbon dioxide or organic acids, it acts upon the lead, converting it into the salt of the acid in question. The hygienic question is, whether drinking water should be conducted through lead pipes. All things considered, it is much safer not to use them, since pipes of other metals are practically unacted upon by water.

Lead does not dissolve appreciably in hydrochloric acid, since its surface becomes quickly covered with a layer of insoluble chloride. It dissolves to some extent in concentrated sulphuric acid, and the sulphate is precipitated when the acid is diluted. Concentrated sulphuric acid which has come in contact with lead during its preparation, almost always contains some lead sulphate in solution. Nitric acid and certain organic acids readily dissolve lead, converting it into the corresponding salt.

Lead is readily precipitated from its salts by a number of metals. This is especially the case with zinc and iron. When a bar of zinc is suspended in a solution of a lead salt, the lead is thrown out and the zinc dissolves. What takes place is a transfer of the electrical charge from the lead ion to the zinc atom, converting the former into an atom and the latter into an ion:—

$$\overset{++}{\mathrm{Pb}}, \overset{-}{\mathrm{N}}\mathrm{O_3}, \overset{-}{\mathrm{N}}\mathrm{O_3} + \mathrm{Zn} = \overset{++}{\mathrm{Zn}}, \overset{-}{\mathrm{N}}\mathrm{O_3}, \overset{-}{\mathrm{N}}\mathrm{O_3} + \mathrm{Pb}.$$

The reason that this takes place is that zinc has an enormous solution-tension and lead a very small solution-tension (see p. 393). The zinc atoms take the charge from the lead ions, becoming themselves ions, and the lead, having lost its charge, is converted into atoms, which are insoluble in water, and the lead is precipitated.

The lead frequently acquires very beautiful, tree-like forms when it separates upon the zinc. This is known as *Arbor Saturni*, or the *lead tree*. Lead forms a few alloys which are of value. *Type metal* consists of 12 parts of lead, 3 parts of tin, and 5 parts of antimony. *Pewter* is an alloy containing 4 parts of lead and 1 part of tin.

Oxides of Lead. — Lead forms a number of compounds with oxygen. *Lead suboxide*, Pb_2O, is formed as the first product of the oxidation of lead, and by decomposing the oxalate at a low temperature.

Lead oxide, PbO, is formed by heating salts of lead, especially the nitrate and carbonate. It is also known as *litharge* or *massicot.*

It is reddish-yellow or brown, depending upon the method of formation. It dissolves slightly in water, forming the corresponding hydroxide, which will be considered a little later.

Minium, Pb_3O_4, is formed by gently heating lead oxide on the air (to 300°–400°). On account of its bright red color it is known as *red lead*. When minium is highly heated, it breaks down into litharge and oxygen. When treated with nitric acid, minium partly dissolves and partly remains behind as lead dioxide. It is regarded as a mixture of $2\,PbO$ and PbO_2.

Lead sesquioxide, Pb_2O_3, is formed by oxidizing an alkaline solution of lead oxide with sodium hypochlorite.

Lead dioxide, PbO_2, is formed by oxidizing the lower oxides of lead by the action of nitric acid upon minium, as we have seen; but very readily by treating a lead salt with bleaching-powder. The reaction with lead nitrate is:—

$$2\,Pb(NO_3)_2 + Ca(OCl)_2 + 2\,H_2O = CaCl_2 + 4\,HNO_3 + 2\,PbO_2.$$

Lead dioxide is also formed when a solution of lead nitrate is electrolyzed. The dioxide separates at the anode.

Like dioxides in general, lead dioxide readily gives up its oxygen, and is, therefore, an excellent oxidizing agent. When boiled with hydrochloric acid, chlorine is evolved as with manganese dioxide. When acidified and treated with hydrogen dioxide, oxygen is evolved from both dioxides:—

$$PbO_2 + H_2O_2 + 2\,HNO_3 = 2\,H_2O + Pb(NO_3)_2 + O_2.$$

Lead dioxide is the anhydride of an acid. When treated with a strong alkali it dissolves, forming salts of the general type M_2PbO_3.

Hydroxides of Lead. — When a lead salt is treated with an alkali, lead hydroxide is precipitated as a white, amorphous mass:—

$$Pb(NO_3)_2 + 2\,KOH = 2\,KNO_3 + Pb(OH)_2.$$

It has basic properties forming salts with strong acids, and also acid properties dissolving readily in strong bases. The salts have the composition M_2PbO_2, and are known as *plumbites*.

The hydroxide corresponding to lead dioxide, $Pb(OH)_4$, also has acid properties, and is known as *normal* or *orthoplumbic acid*. The *metaplumbic acid* is obtained from the ortho acid by the loss of one molecule of water:—

$$Pb(OH)_4 = H_2O + H_2PbO_3.$$

Salts of both of these acids are known as *plumbates*. We have the calcium and potassium salts Ca_2PbO_4, K_2PbO_3, etc. The lead

salts of these acids, Pb_2PbO_4 and $PbPbO_3$, are the well-known oxides Pb_3O_4 and Pb_2O_3.

Chlorides of Lead. — Lead generally forms the bivalent ion $\overset{++}{Pb}$, which readily combines with the anions of acids, forming salts that are beautifully crystallized. It also forms the tetravalent ion $\overset{++++}{Pb}$, which can combine with certain anions of acids and form salts; but these are unstable. This is what we would expect, since we have just seen that tetravalent lead and even bivalent lead can manifest acid properties.

Lead chloride, $PbCl_2$, is readily formed by bringing together lead ions $\overset{++}{Pb}$ and chlorine ions $\overset{-}{Cl}$: —

$$\overset{++}{Pb}, \overset{-}{NO_3}, \overset{-}{NO_3} + \overset{-}{Cl}, \overset{+}{Na} + \overset{-}{Cl}, \overset{+}{Na} = \overset{+}{Na}, \overset{-}{NO_3} + \overset{+}{Na}, \overset{-}{NO_3} + PbCl_2.$$

Lead chloride is a white, crystalline substance, somewhat soluble in hot water, but only slightly soluble in cold water. Lead forms a *tetrachloride*, $PbCl_4$, but not by any direct method. When lead dioxide is dissolved in the most concentrated hydrochloric acid at a low temperature, and ammonium chloride added to the solution, a yellow salt is obtained having the composition $(NH_4)_2PbCl_6$. When this salt is treated with concentrated sulphuric acid, the following reaction takes place: —

$$(NH_4)_2PbCl_6 + H_2SO_4 = (NH_4)_2SO_4 + H_2PbCl_6.$$

The *hydrochlorplumbic acid* decomposes at once into hydrochloric acid and lead tetrachloride: —

$$H_2PbCl_6 = 2\,HCl + PbCl_4.$$

Lead tetrachloride is very unstable, breaking down into lead chloride and chlorine. It solidifies at $-15°$ and is strongly hydrolized by water, forming lead dioxide and hydrochloric acid.

Iodide of Lead, PbI_2, is an especially beautiful substance. It is formed by the action of a soluble iodide on a soluble lead salt: —

$$Pb(NO_3)_2 + 2\,KI = 2\,KNO_3 + PbI_2.$$

It crystallizes from hot water and acetic acid in unusually beautiful, glistening, yellow plates.

Lead Nitrate, $Pb(NO_3)_2$, is formed by the action of dilute nitric acid on lead. It is not very soluble in strong nitric acid, and, therefore, the strong acid acts less vigorously upon the lead than the weak. It is one of the few lead salts which are readily soluble in water.

Lead Sulphide, PbS, occurs in nature, as we have already seen, as galena. It is formed whenever bivalent lead ions come in contact with sulphur ions — whenever a soluble lead salt is treated with hydrogen sulphide: —

$$Pb(NO_3)_2 + H_2S = 2\,HNO_3 + PbS.$$

Lead sulphide is a black solid only slightly soluble in dilute acids. Lead, therefore, belongs to those metals whose sulphides are precipitated from neutral salts by hydrogen sulphide.

Lead Sulphate, $PbSO_4$, occurs in nature as *anglesite* or lead vitriol. It is isomorphous with heavy spar or barium sulphate. It is formed whenever lead, $\overset{++}{Pb}$, ions come in contact with sulphuric, $\overset{=}{SO_4}$, ions. It is very insoluble in water, and is, therefore, formed whenever a soluble sulphate is added to a soluble lead salt: —

$$Pb, \overset{-}{NO_3}\,\overset{-}{NO_3} + \overset{+}{K}, \overset{+}{K}, \overset{=}{SO_4} = \overset{+}{K}, \overset{-}{NO_3} + \overset{+}{K}, \overset{-}{NO_3} + PbSO_4.$$

Lead Persulphate, $Pb(SO_4)_2$, or the lead salt of persulphuric acid, is formed by electrolyzing strong sulphuric acid between electrodes of lead.

Lead Carbonate, $PbCO_3$. — The carbonate of lead is an important compound, and especially the basic carbonates. The normal carbonate occurs in nature as *cerussite*, and is isomorphous with aragonite, a form of calcium carbonate. The normal carbonate is formed when ammonium carbonate is added to a solution of lead nitrate: —

$$Pb(NO_3)_2 + (NH_4)_2CO_3 = 2\,NH_4NO_3 + PbCO_3.$$

If any other alkaline carbonate is used, such as sodium carbonate, a *basic lead carbonate* is precipitated, and this is extensively used as a pigment under the name of *white lead.*

The old Dutch method of making white lead consists in placing sheet lead, rolled into spirals, in porcelain pots containing a little vinegar. The latter did not touch the lead. The vessels were then placed in horse-manure, which decomposed and furnished the necessary amount of carbon dioxide. The lead plates became covered in time with a layer of basic lead carbonate, which was removed mechanically.

This method, which consumed much time, has now given place to some extent to quicker processes. Normal lead acetate is shaken with litharge and water, when the basic acetate is formed. This is then treated with carbon dioxide, when basic lead carbonate is formed. The ordinary white lead which is used as a pigment is a

mixture of basic carbonates of different composition. It must never be used in painting objects which are exposed to the action of hydrogen sulphide, since it will turn black, due to the formation of lead sulphide.

Lead Chromate, $PbCrO_4$, is formed whenever lead ions, $\overset{++}{Pb}$, and chromic ions, $\overset{=}{CrO_4}$, come together: —

$$\overset{++}{Pb}, \overset{-}{NO_3}, \overset{-}{NO_3} + \overset{+}{K}, \overset{+}{K}, \overset{=}{CrO_4} = \overset{+}{K}, \overset{-}{NO_3} + \overset{+}{K}, \overset{-}{NO_3} + PbCrO_4.$$

The yellow lead chromate is difficultly soluble in water, and is used as a pigment — *chrome yellow*. The basic chromate is yellowish red and is known as *chrome orange*.

Lead chromate is also formed when a soluble lead salt is treated with a soluble dichromate, since the chromate of lead is insoluble and the dichromate soluble: —

$$2\,Pb(NO_3)_2 + K_2Cr_2O_7 + H_2O = 2\,PbCrO_4 + 2\,KNO_3 + 2\,HNO_3.$$

Lead Acetate, $Pb(CH_3COO)_2\,3\,H_2O$, is an important soluble salt of lead. It is formed by the action of acetic acid on lead oxide or finely divided lead. On account of its sweet taste it is known as *sugar of lead*. As we have seen, the acetate is an important intermediate product in the formation of basic lead carbonate, the latter being formed when carbon dioxide is passed through a solution of the acetate or basic acetate.

Basic acetates are formed when lead oxide is dissolved in normal acetates. In contradistinction to sugar of lead, these are known as *vinegar of lead*.

The Storage Battery or Accumulator. — One of the most important uses of lead to-day, is in connection with the form of an electrical battery know as the storage battery or accumulator. When a plate of lead and one of lead dioxide are dipped into sulphuric acid, and connected externally, we have a cell which is capable of furnishing considerable electrical energy. Such a cell is formed by passing an electric current between the lead plates covered with lead sulphate, and immersed in sulphuric acid. The sulphate at the one plate is reduced to lead, which is deposited upon that plate, and at the other oxidized to lead dioxide, which is deposited upon the second plate. We have thus converted electrical energy into chemical or intrinsic energy. When the "charging current" is interrupted and the cell closed, an electric current flows in the direction opposite to that used in charging the cell. While the "discharging current" is flowing, the lead at the one plate and the lead dioxide at the other are con-

verted into lead sulphate. The electrical energy produced comes from the chemical energy which disappears. The chief source of the electromotive force in a storage or secondary battery is the transformation of quadrivalent lead ions $\overset{++++}{Pb}$, into bivalent lead ions $\overset{++}{Pb}$. The quadrivalent ions are furnished continually by the lead dioxide. They pass into bivalent ions, giving up two electrical charges, and form with the sulphuric ions, $\overset{=}{SO_4}$, lead sulphate. By means of these reciprocal transformations of lead, lead sulphate, and lead dioxide, it is possible to convert electrical energy into chemical, or "store" it as we say; and then to reconvert the chemical or intrinsic energy into electrical energy at will. The great weight of the lead plates is a serious disadvantage in the storage battery, and an attempt is now being made to use iron and nickel instead of lead.

TIN (At. Wt. = 119.0)

An element chemically allied to lead, but differing from it in many respects, is tin. This metal is useful on account of its chemical inactivity, and is valuable on account of its properties and because it does not occur in large quantities. Tin occurs in the uncombined condition along with gold, but chiefly as tin dioxide, SnO_2, known as *tinstone* or *cassiterite.* The chief localities for tin are Cornwall in England, Siberia, and the East India Islands.

Preparation and Properties of Tin. — The sulphur, arsenic, and similar impurities are removed from the tin ore by roasting, and the oxide is then roasted with carbon. The oxide is readily reduced to the metal, and this is purified by repeated melting; the molten tin being poured off from the less easily fusible alloys. The purest tin comes from the island of Banca, and is known as *Banca tin.* Another comparatively pure form is known as *block-tin.*

Tin is light in color and quite soft. It can be readily hammered or rolled into thin sheets known as tin-foil, which is used for covering objects to protect them from the action of air, moisture, etc. It is crystalline, and the movement of the crystals over one another produces a crackling noise known as the *cry of tin.* Tin melts at 233° and volatilizes at 1500°. It has a specific gravity of 7.3. While tin is malleable at ordinary temperatures it becomes brittle above 200°. Tin is not very readily attacked by reagents. It is not acted on chemically by the air or moisture. It dissolves in concentrated hydrochloric and sulphuric acids, forming the corresponding salts. Concentrated nitric acid oxidizes tin to metastannic acid. Tin dissolves in caustic alkalies, forming salts of stannic acid. On

account of its resistance to ordinary reagents tin is frequently used for covering objects which are to be used in the kitchen, or vessels for holding fruit or water. Indeed, in distilling water block-tin condensers are frequently employed, since water-vapor is practically without influence upon them. Iron objects are plated with tin by first cleansing them by washing with an acid, and then dipping them into molten tin.

Allotropic Forms of Tin. — Tin occurs in allotropic modifications. At ordinary temperatures the white modification with which we are so familiar is the stable form. Cohen showed that below 20° the white modification is unstable, and this passes over slowly into a gray modification which is the stable form at low temperatures. The transformation temperature is 20°. Just below this temperature the gray modification is formed slowly; the velocity of the transformation into the gray modification increasing until a temperature of − 48° is reached. The velocity of the transformation into *gray tin* at temperatures slightly below 20° is increased by the presence of a little gray tin or pink salt, $SnCl_4 . 2 NH_4Cl$. Gray tin is brittle, readily crumbling to powder, and has a smaller specific gravity (5.8) than white tin. This explains the crumbling of tin known as *tin-pest*, which occurs in tin organ pipes and other tin objects in cold countries.

The brittle modification of tin which exists at elevated temperatures is probably another allotropic form.

Alloys of Tin. — Molten tin dissolves readily in most of the other metals in the molten condition, and forms a large number of alloys with them. Some of these are very important substances. *Soft solder* is an alloy of tin and lead. The *bronzes*, as has already been stated, are alloys of tin. *Mannheim gold* is an alloy of zinc, copper, and tin. *Britannia metal* is an alloy of tin and antimony, containing one part of antimony to nine of tin. Tin readily forms an *amalgam* with mercury, and this is used for plating glass mirrors. Tin-foil is coated with mercury and a glass plate placed upon it. The tin amalgam which is formed adheres tightly to the glass. This method of making mirrors is being rapidly abandoned and silvered surfaces used instead, as has already been mentioned.

The Tin Ions. — The element tin forms two kinds of ions, those which are bivalent, $\overset{++}{Sn}$, and those which are quadrivalent, $\overset{++++}{Sn}$. Of these the quadrivalent ion is the more stable, the bivalent tending to pass over into it. No other ion of tin is known. The stannous ions passing over into the stannic, take up readily two electrical charges, or are good reducing agents, as we say.

Stannous (SnO) and Stannic (SnO_2) Oxides. — The two oxides corresponding to the stannous and stannic conditions are known. *Stannous oxide*, SnO, formed by heating stannous hydroxide in a current of carbon dioxide, is comparatively unstable, readily combining with oxygen and forming stannic oxide, SnO_2. *Stannic oxide*, SnO_2, occurs in nature as *tinstone.* It is also readily prepared by burning tin in the air. Tin dioxide can be obtained in a number of crystalline forms.

Stannous ($Sn(OH)_2$) and Stannic ($Sn(OH)_4$) Hydroxides. — Stannous hydroxide is precipitated from stannous salts by the addition of an alkali: —

$$SnCl_2 + 2\,NaOH = 2\,NaCl + Sn(OH)_2.$$

Stannous hydroxide readily dissolves in an excess of the alkali, forming salts. These, however, are unstable, readily passing over into salts where the tin is tetravalent, metallic tin separating from the solution.

Stannic Hydroxide, $Sn(OH)_4$, is formed by treating tin with nitric acid of medium concentration. It readily loses water, forming *metastannic acid,* H_2SnO_3, which is soluble in alkalies forming *metastannates.* Metastannic acid is insoluble in water, and also in acids.

Another compound having the composition H_2SnO_3 is known, which is soluble in acids. It is formed by boiling stannic chloride with water, or by treating stannic chloride with ammonia. It is also formed by treating the potassium salt with an equivalent of an acid: —

$$K_2SnO_3 + 2\,HCl = 2\,KCl + H_2SnO_3.$$

It dissolves readily in alkalies forming salts, which are known as *stannates.* To distinguish it from the isomeric metastannic acid, it is known as *stannic acid.* The latter passes over slowly into the former.

Stannous Chloride, $SnCl_2 . 2\,H_2O$. — The best-known stannous salt is the chloride, $SnCl_2$. It is formed by dissolving tin in hydrochloric acid, also by heating tin in a current of dry hydrochloric acid gas. Stannous chloride crystallizes with two molecules of water. It melts at 250° and boils at 610°. On account of the marked tendency of the stannous ion to pass over into the stannic, it readily undergoes superficial oxidation. On account of this same tendency, stannous chloride is an excellent reducing agent, and is frequently used where mild reductions are desired, especially in organic chemistry. It combines readily with chlorine, as we would expect, forming stannic chloride. So great is this power that it removes the

chlorine from the chlorides of mercury, precipitating metallic mercury: —

$$HgCl_2 + SnCl_2 = Hg + SnCl_4,$$
$$2\,HgCl + SnCl_2 = 2\,Hg + SnCl_4.$$

Stannous chloride combines directly with free chlorine, forming stannic chloride: —

$$\overset{++}{Sn}, \overset{-}{Cl}, \overset{-}{Cl} + Cl_2 = \overset{++++}{Sn}, \overset{-}{Cl}, \overset{-}{Cl}, \overset{-}{Cl}, \overset{-}{Cl}.$$

This is another example of that mode of ion formation where a cation takes on more positive electricity, at the same time converting an atom into an anion.

Stannous chloride combines also with hydrochloric acid, forming *hydrochlorstannous acids*. The salts of two such acids are well known, and show that the acids have the compositions $HSnCl_3$ and H_2SnCl_4. Stannous chloride is known commercially as *tin-salt*.

Stannic Chloride, $SnCl_4$. — The tetrachloride is formed, as we have seen, by the action of mercuric chloride on stannous chloride or on metallic tin. It is also formed by the direct action of chlorine gas on tin. It is a liquid boiling at 114°, and fuming in contact with the air. It is known as *spiritus fumans Libavii*. When brought in contact with a little water, it forms a viscous mass known as *tin-butter*, having the composition $SnCl_4 . 3\,H_2O$. With much water stannic chloride is readily hydrolyzed, forming the hydroxide and hydrochloric acid. The hydrochloric acid set free as the result of the comparatively slow hydrolysis, produces the rapidly increasing conductivity which is observed when stannic chloride is dissolved in water. Stannic chloride combines directly with hydrochloric acid, forming hydrochlorstannic acid, $H_2SnCl_6 . 6\,H_2O$, which can be obtained in the free condition. Salts of this acid can be obtained by bringing alkaline chlorides in contact with stannic chloride. The ammonium salt, $(NH_4)_2SnCl_6$, is known in commerce as *pink salt*.

Sulphides of Tin. — Stannous sulphide, SnS, is formed by conducting hydrogen sulphide into a solution of stannous chloride: —

$$SnCl_2 + H_2S = 2\,HCl + SnS.$$

Stannous sulphide is a brownish-black powder, insoluble in dilute acids, but soluble in ammonium polysulphide, forming ammonium *sulphostannate*, in which the tin is in the quadrivalent condition: —

$$SnS + (NH_4)_2S_2 = (NH_4)_2SnS_3.$$

Stannous sulphide is also formed by melting tin with sulphur.

Stannic sulphide is precipitated as a light yellow powder when hydrogen sulphide is passed into a solution of a stannic salt or a stannate: —

$$SnCl_4 + 2\,H_2S = 4\,HCl + SnS_2.$$

It may also be prepared by heating together tin, sulphur, and ammonium chloride. Prepared by the latter method it is crystalline, and has a golden-yellow color; it is known as *mosaic gold* and used as a pigment and for gilding.

Stannic sulphide dissolves readily in ammonium sulphide, forming *sulphostannates* or *thiostannates*: —

$$SnS_2 + (NH_4)_2S = (NH_4)_2SnS_3.$$

This reaction is of importance in the separation of tin from most of the elements. It will be remembered that in addition to tin, the sulphides of only arsenic, antimony, gold, and platinum are soluble in yellow ammonium sulphide. By this reaction arsenic, antimony, tin, gold, and platinum are separated from the remaining elements.

CHAPTER XLI

I. **RUTHENIUM**	**RHODIUM**	**PALLADIUM**
II. **OSMIUM**	**IRIDIUM**	**PLATINUM**

Although classed together these two groups of three elements each have certain properties which are markedly different. The most striking is the atomic weights. The first three have atomic weights which are not widely removed from one hundred, while the atomic weights of the last three are not widely removed from two hundred. Similarly, the specific gravity of the first three elements is close to twelve, while the specific gravity of the last three is about twenty-two. We shall take up first the lighter elements,— ruthenium, rhodium, and palladium.

RUTHENIUM (At. Wt. = 101.7)

Ruthenium occurs in nature with platinum. When the platinum is dissolved in *aqua regia*, ruthenium remains behind undissolved.

Ruthenium was discovered in 1845 by the German chemist Claus. The metal is steel-gray in color and has a specific gravity of 12.2. It fuses only at very high temperatures, certainly not below 1800°.

Ruthenium combines with oxygen, forming the compounds RuO, Ru_2O_3, RuO_2, RuO_3, and RuO_4. The higher oxides are anhydrides of acids, which will be referred to a little later.

Ruthenium is quite resistant to *aqua regia*, but combines with chlorine, forming three compounds,— $RuCl_2$, $RuCl_3$, and $RuCl_4$.

The trichloride combines with hydrochloric acid, forming H_2RuCl_5, and the tetrachloride with hydrochloric acid, forming H_2RuCl_6.

Ruthenium dissolves in fused caustic potash, forming two classes of salts. When fused with potash and potassium nitrate, *potassium ruthenate*, K_2RuO_4, is produced. This salt forms dark crystals which dissolve, and give a deep orange-colored solution. When the ruthenate is treated with a dilute acid it passes over into the perruthenate $KRuO_4$. In the ruthenates and perruthenates we have obviously the analogues of the manganates and permanganates.

RHODIUM (At. Wt. = 103.0)

The element rhodium occurs in very small quantities, and usually with platinum and gold. It has unusually valuable properties, melting higher than platinum and being unacted upon by acids and even by *aqua regia.* When platinum is alloyed with a considerable quantity of rhodium, it becomes much more resistant to chemical reagents. An alloy of platinum and rhodium, containing from 30 to 40 per cent of rhodium, is not acted upon by *aqua regia.* Such an alloy fuses higher than platinum, and is more valuable than pure platinum.

Rhodium acts mainly as a trivalent element, forming such compounds as $Rh(OH)_3$, $RhCl_3$, etc. Rhodium also forms characteristic double chlorides of the type M_3RhCl_6, where M is an alkali metal.

PALLADIUM (At. Wt. = 106.5)

Palladium occurs with platinum, but the chief source of palladium is a gold ore in Brazil. The ore is fused with silver and then treated with nitric acid. The silver and palladium dissolve, and the silver is separated from the palladium by precipitation, as the chloride. The palladium can then be precipitated as the cyanide, which is ignited or thrown out of the solution directly with metallic zinc.

To chemical reagents, palladium is the least resistant of all the platinum metals. It dissolves readily in nearly all of the strong acids. It is white like silver and fuses at about 1500°, which is lower than any of the other platinum metals.

Palladium is best known chemically in connection with its remarkable power to *absorb hydrogen gas.* Metallic palladium at 100° can absorb more than 800 volumes of hydrogen gas. It has been supposed for a long time that there was a compound formed having the composition Pd_2H and known as *palladium hydride.* Some doubt has recently been thrown upon the existence of such a compound by studying the absorption of hydrogen by palladium in terms of the phase rule.

Palladium absorbs more than 600 volumes of hydrogen, which would correspond to the formation of this compound, but this may be simply a solution of hydrogen in the supposed compound Pd_2H. Van't Hoff has shown that if hydrogen under increased pressure is brought in contact with palladium hydride, the hydrogen is absorbed in terms of Henry's law, *i.e.* proportional to the pressure of the gas. This he has cited as an excellent example of a solid solution of a gas in a solid, — hydrogen in palladium hydride.

Palladium hydride readily gives up its hydrogen to substances which can be reduced, and is, therefore, an excellent reducing agent. The halides are reduced by it to the corresponding acids.

Palladium hydride gives up all of its hydrogen when heated for a time to a red heat.

Palladium forms the *oxides* PdO and PdO_2. It also forms the *chlorides* $PdCl_2$ and $PdCl_4$. These are typical of the palladous and palladic compounds. In the former the palladium is bivalent and in the latter tetravalent.

Palladic chloride may be regarded as combining with hydrochloric acid and forming *hydrochlorpalladic acid*, H_2PdCl_6. This compound is formed when palladium is dissolved in an excess of *aqua regia*. Salts of this acid are obtained by treating palladic chloride with the chloride of an alkali: —

$$PdCl_4 + 2\,KCl = K_2PdCl_6.$$

The potassium and also the ammonium palladic chlorides are only slightly soluble in water. In this respect, as well as in their composition, they resemble the corresponding compounds of platinum, as we shall see.

OSMIUM (At. Wt. = 191.0)

We now come to the three heavy metals of the platinum group. The first of these, osmium, has the specific gravity 22.5, and is, therefore, the heaviest of all known elements. It occurs in platinum ores as an alloy with iridium. When these ores are treated with *aqua regia*, neither the iridium nor the osmium dissolves. Osmium like ruthenium forms a volatile oxide, OsO_4, and this property is utilized to separate osmium from iridium.

Osmium is characterized by its high melting-point. It does not melt at the highest temperatures thus far produced, and attempts have been made to substitute osmium wire for the carbon filament in the electric light. The alloy of osmium with iridium finds applications on account of its resistance to chemical reagents, and on account of its hardness and resistance to mechanical abrasion.

Heated in contact with the air, osmium combines with oxygen, forming *osmium tetroxide* (OsO_4), which is easily volatile at 100°. It is easily reduced by organic matter to metallic osmium, and is, therefore, used in the preparation of microscopic sections of tissues. For the same reason it is very poisonous when inhaled, producing great irritation of the mucous membrane of the eyes, nose, and throat. The aqueous solution of osmium tetroxide is perfectly neutral, and the compound has been erroneously called osmic acid. *Osmium forms*

salts of the composition M_2OsO_4, but the corresponding oxide, OsO_3, is not known.

Osmium combines with chlorine, forming the *dichloride*, $OsCl_2$, and the *tetrachloride*, $OsCl_4$. Osmium also forms salts of the general composition M_2OsCl_6.

IRIDIUM (At. Wt. 193.0)

Iridium occurs, as already mentioned, along with osmium as *osmium-iridium* in platinum ores. It is also combined, in part, with the platinum as *platinum-iridium*. The separation of osmium from iridium has already been referred to. Iridium is separated from platinum by dissolving the two in *aqua regia*, and adding ammonium chloride. A double chloride of iridium and ammonium, $(NH_4)_2IrCl_6$, is formed, which is readily soluble in water, but not in water saturated with ammonium chloride. Metallic iridium is light in color, and does not melt until the temperature of the flame of the oxyhydrogen blowpipe is reached. It has a specific gravity of 22.4, and is, therefore, next to osmium, the heaviest of all known elements.

Iridium is more resistant to chemical reagents than platinum, and alloys of iridium and platinum are used, instead of pure platinum, for making chemical apparatus such as crucibles, dishes, etc. The standard metre in Paris consists of 90 per cent platinum and 10 per cent iridium; and this particular alloy has been found, on the whole, to be the best in preparing measuring apparatus.

Iridium is insoluble in even the strongest mineral acids, and dissolves slowly in *aqua regia* only when in the finely divided condition.

Iridium acts toward oxygen as a trivalent and quadrivalent element, forming the oxides Ir_2O_3 and IrO_2. The corresponding hydroxides, $Ir(OH)_3$, and $Ir(OH)_4$, are known. Iridium combines with chlorine, forming the compounds $IrCl_2$, $IrCl_3$, and $IrCl_4$. Towards chlorine it, therefore, acts as a bivalent, trivalent, and quadrivalent element. Like the other members of the platinum group, iridium forms chloro acids and alkali salts of these acids. Thus we have M_2IrCl_6, in which the ion, $\overset{=}{Ir}Cl_6$, is bivalent, and also M_3IrCl_6, in which the ion, $\overset{\equiv}{Ir}Cl_6$, is trivalent. Ammonia forms with iridium as with the other platinum metals complex compounds.

PLATINUM (At. Wt. = 194.8)

Platinum, one of the most valuable elements from the standpoint of chemistry on account of its power to resist chemical reagents,

occurs fairly widely distributed, but not in large quantities. The countries in which platinum occurs in the greatest quantity are California, Borneo, and the Ural Mountains. It occurs in company with the other platinum metals, and is separated from them by methods with which we are now more or less familiar.

Properties of Platinum. — Platinum is light in color, has a specific gravity of 21.4, and melts at about 1770° in the flame of the oxy-hydrogen blowpipe. It is both ductile and malleable — can be drawn into thin wire and hammered into thin sheets.

Platinum can exist in a number of physical conditions. In addition to ordinary white platinum, which is very compact and metallic in all of its properties, we know platinum in the form of a spongy mass which is known as *platinum sponge*. Platinum is obtained in this condition when the chloride of ammonium and platinum, which will be referred to a little later, is heated. Platinum sponge has a gray color, and differs fundamentally from the black variety of platinum known as *platinum black*. This is obtained by reduction of platinum compounds. When both of these varieties are highly heated and subjected to pressure, they pass back into ordinary white platinum. Finely divided platinum has a remarkable power to absorb oxygen. It can absorb several hundred volumes of oxygen, and the oxygen in this condition is very active chemically, readily effecting oxidations. In a similar manner it can absorb considerable quantities of hydrogen, and the hydrogen under these conditions has strongly reducing properties.

This power of platinum to absorb gases, and to produce chemical combinations between them, can be readily illustrated by means of a piece of platinum foil and a gas-jet. Ignite the jet and heat the platinum to redness. Then extinguish the jet until the platinum ceases to glow. If now the gas-jet is turned on again and the gas allowed to flow over the surface of the hot, but not incandescent platinum, it will be ignited again. This experiment can be repeated as often as desired with the same piece of platinum.

The power of platinum to absorb gases and produce chemical reaction catalytically is also illustrated by a *form of lamp devised by Davy*. An ordinary spirit lamp is filled with a mixture of alcohol and ether and ignited. A spiral of platinum wire is suspended in the flame and heated to incandescence. The flame is then extinguished until the spiral ceases to glow. If the vapors of alcohol and ether are now allowed to fall again on the hot platinum, the latter will again become incandescent and ignite the lamp.

The *Döbereiner lamp*, constructed early in the nineteenth century, is based upon the same principle. A current of hydrogen is allowed to flow over spongy platinum, when it combines so rapidly with oxygen that the platinum is heated to incandescence and ignites the hydrogen.

Chemically, platinum is very resistant to reagents, and upon this fact its value chiefly depends. It is not attacked appreciably by any of the strong mineral acids, but dissolves in aqua regia. It, however, dissolves in the fused alkalies, cyanides, etc. Platinum must not be heated in contact with carbon, since some of the carbon dissolves and makes the platinum brittle. Special precaution must be taken not to heat a mixture of carbon and sand in platinum vessels, since the platinum combines with the silicon, forming a brittle substance. Similarly, phosphates must not be heated in platinum vessels along with a reducing agent, since platinum readily combines with phosphorus. Platinum readily forms alloys with the heavy metals, such as lead, mercury, etc. Such substances must never be heated in platinum apparatus.

Uses of Platinum. — Platinum is especially useful to the chemist on account of its resistance to chemical reagents. It is not attacked appreciably by the strongest acids, not even by hydrofluoric acid. It is also not attacked by the fused alkaline carbonates. Platinum vessels can thus be used where even porcelain could not be employed. On account of its high melting-point platinum is used for holding substances which are to be heated to a high temperature. Since it does not volatilize in the flame of the Bunsen burner it does not impart any color to the flame, and is therefore useful in spectrum analysis to hold the substance whose spectrum it is desired to study. A platinum wire is made into a loop and dipped into the substance in question. It is then inserted into the flame, when only the spectrum which is characteristic of the substance appears.

Platinum does not dissolve in acids on account of its low solution-tension, and on account of this same property it does not pass into solution when made the pole of an electric current. Platinum is, therefore, used as electrodes in affecting electrolysis where it is desired to separate the metals quantitatively and determine the amounts which are present.

Platinum finds extensive use in almost every phase of gravimetric analysis. On account of its high fusion- and boiling-points it has no appreciable vapor-tension, even at the temperature of the blast-lamp. When it is desired to heat precipitates to a high temperature platinum crucibles are frequently employed.

Platinum finds to-day extensive applications in the arts. Platinum has nearly the same temperature coefficient of expansion as glass, and almost exactly the same as red and blue fusion glass. If it is desired to seal an electrical connection through glass a platinum wire is the most convenient means. This fact is utilized not only in constructing standard cells, but also incandescent electric lights. Large amounts of platinum are used in this way.

Platinum is also used in the form of fine wire to draw together the tops of the mantles in the Welsbach burner. It is also employed in constructing stills for concentrating sulphuric acid, and as a catalyzing agent in the new method of making sulphuric acid. In contact with platinized asbestos, sulphur dioxide combines with oxygen at the elevated temperature forming sulphur trioxide.

Colloidal Solution of Platinum. — A pseudosolution or colloidal solution of platinum can readily be prepared by a method recently discovered by Bredig. When two bars of platinum are dipped into water, so that their lower ends are close together, but do not touch, as shown in Fig. 43, and an electric current of 8–12 amperes and 30–40 volts passed through the circuit, the platinum is torn off of the bars in such a fine state of division that the solution appears perfectly homogeneous, when examined under the most powerful microscope. That the platinum is not in a state of true solution, is shown by the fact that it does not lower the freezing-point or vapor-tension of the solvent. Such solutions, which have been prepared not only of platinum, but of gold, silver, cadmium, iridium, etc., have been studied extensively by Bredig, especially in the cases of platinum, gold, and silver. These pseudosolutions of the heavy metals have been found to have some remarkable properties in connection with their catalytic action, especially as effecting the decomposition of hydrogen dioxide. Analogies between the action of these solutions and organic enzymes have been pointed out and established experimentally, which are undoubtedly deep-seated. Without going into detail in this subject, it may be said that infinitesimal quantities of the same substances which poison the organic enzymes, also "poison" the colloidal solutions of the metals, preventing or greatly hindering

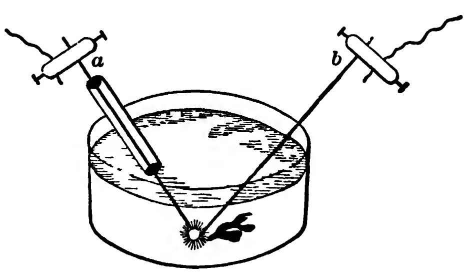


FIG. 43.

their catalytic activity. A number of other analogies have been shown to exist.

Oxides and Hydroxides of Platinum.—Platinum forms two oxides, PtO and PtO_2, which are derived from the corresponding hydroxides, $Pt(OH)_2$ and $Pt(OH)_4$, by careful heating. The hydroxides are obtained from the platinous and platinic chlorides, or from the double chlorides with the alkalies, by the action of a base. All of these substances are unstable at elevated temperatures, breaking down and yielding metallic platinum.

Chlorides of Platinum.—Platinum forms two chlorides—platinous chloride, $PtCl_2$, in which the platinum is bivalent, $\overset{++}{Pt}$, and platinic chloride, in which the platinum is tetravalent, $\overset{++++}{Pt}$.

Platinous chloride is obtained by heating platinum sponge to 250° in chlorine gas. It is a green powder which is insoluble in water. When treated with hydrochloric acid it dissolves forming *hydrochlorplatinous acid*, H_2PtCl_4. When this compound is heated to 300° it breaks down into hydrochloric acid and platinous chloride. This acid is also produced by reducing hydrochlorplatinic acid, H_2PtCl_6, the latter losing two atoms of chlorine and passing over into the former. Salts of hydrochlorplatinous acid are known. These have the composition M_2PtCl_4. The chlorplatinous ion $\overset{=}{PtCl_4}$ is, therefore, bivalent.

Platinic chloride, $PtCl_4$, is obtained by carefully heating hydrochlorplatinic acid to 350° in the presence of chlorine. It is not obtained by dissolving platinum in *aqua regia*. Platinic chloride, which is quite soluble in water, readily combines with hydrochloric acid forming *hydrochlorplatinic acid*, H_2PtCl_6. This same compound is formed when platinum is dissolved in aqua regia.

Many salts of this acid are known. We have already seen that the potassium and ammonium chlorplatinates, K_2PtCl_6 and $(NH_4)_2PtCl_6$, are difficultly soluble in water, while the sodium salt, Na_2PtCl_6, is readily soluble. This reagent thus enables us to separate sodium from potassium. It is also very important in connection with the quantitative determination of potassium, since potassium chlorplatinate is almost completely insoluble in a mixture of water and alcohol. The calcium and rubidium salts of this acid are even less soluble than the potassium and ammonium compounds.

In this acid the chlorplatinic ion, $\overset{=}{PtCl_6}$, is bivalent, and this is another example of a metal forming part of an anion. When a solution of this acid is electrolyzed the platinum passes to the anode and not to the cathode. We have met with a number of similar cases.

Platinum in the bivalent condition forms a double nitrite with the alkaline nitrites, which is analogous in composition to the alkali platinous chlorides. Thus, when potassium platinous chloride is allowed to remain in contact for a time with potassium nitrite, the following reaction takes place: —

$$K_2PtCl_4 + 4\,KNO_2 = K_2Pt(NO_2)_4 + 4\,KCl.$$

The compound $K_2Pt(NO_2)_4$ is known as *potassium platinonitrite.*

Sulphides of Platinum. — Platinum forms the two sulphides, PtS and PtS_2, as we would expect. These are obtained by precipitating platinous and platinic solutions by means of hydrogen sulphide. When heated these compounds lose sulphur, and metallic platinum is formed.

Double Cyanides of Platinum. — Platinum forms a number of double cyanides, which are characterized by their unusually beautiful color and fluorescence. They can all be regarded as compounds of platinous cyanide, $Pt(CN)_2$, with the cyanide of the element in question. The acid of which these substances are salts, $H_2Pt(CN)_4$, can be obtained by treating the barium salt with sulphuric acid. The potassium salt, $K_2Pt(CN)_4 . 3\,H_2O$ is formed by adding platinous chloride to potassium cyanide.

Two compounds which are characterized by their unusual beauty are the double cyanides of barium and magnesium. Barium platinous cyanide, $BaPt(CN)_4 . 4\,H_2O$, is formed by passing hydrocyanic acid into water containing a mixture of barium carbonate and platinous chloride. It is light yellow in color, with a beautiful play of greenish-violet light over the surface as the crystals are turned. This compound which converts ultra-violet radiation into visible light, and is, therefore, fluorescent, has come into prominence recently in connection with the study of Röntgen rays. It transforms these, and also the radiation given off by uranium, into visible radiations, and has been used in the preparation of screens upon which Röntgen rays are allowed to fall that their presence might be detected by the eye.

The magnesium platinous cyanide, $MgPt(CN)_4$, is remarkable for its color. It can be formed by treating an aqueous solution of the barium salt with a solution of magnesium sulphate. It crystallizes in red prisms. It has a bright green lustre, so that when the sides are observed in reflected light they appear green, while the ends are blue.

It is questionable whether another compound of equal beauty is known in the whole field of chemistry.

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